

# **WORKSHOP PROGRAM AND ABSTRACTS**



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**Workshop on  
Oxygen in the Terrestrial Planets**

**July 20-23, 2004  
Santa Fe, New Mexico**

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Lunar and Planetary Institute  
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National Science Foundation

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## **Preface**

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This volume contains abstracts that have been accepted for presentation at the Workshop on Oxygen in the Terrestrial Planets, July 20–23, 2004, Santa Fe, New Mexico.

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# Program

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**Tuesday, July 20, 2004**

## **WELCOME AND INTRODUCTION**

**8:30 a.m. Kachina Ballroom**

Jones J. \*

*Welcome and Introductory Remarks*

## **METHODS AND TECHNIQUES FOR DETERMINING REDOX STATE**

**8:45 a.m. Kachina Ballroom**

**Chair: K. Righter**

McCanta M. C. \* Rutherford M. J.

*The Calibration of the Pyroxene Eu-Oxybarometer for the Martian Meteorites*

Musselwhite D. S. \* Jones J. H. Shearer C.

*Oxygen Fugacity of the Martian Mantle from Pigeonite/Melt Partitioning of Samarium, Europium and Gadolinium*

Sutton S. R. \* Karner J. M. Papike J. J. Delaney J. S. Shearer C. K. Newville M. Eng P.

Rivers M. Dyar M. D.

*Oxygen Barometry Using Synchrotron MicroXANES of Vanadium*

Papike J. J. \* Karner J. M. Shearer C. K.

*Comparative Planetary Mineralogy:  $V/(Cr+Al)$  Systematics in Chromite as an Indicator of Relative Oxygen Fugacity*

Righter K. \* Sutton S. R. Newville M.

*Micro-XANES Measurements on Experimental Spinels and the Oxidation State of Vanadium in Spinel-Melt Pairs*

Canil D. \* Thom J.

*Plagioclase-Liquid Trace Element Oxygen Barometry and Oxygen Behaviour in Closed and Open System Magmatic Processes*

**12:00-1:30      Lunch**

**Tuesday, July 20, 2004**

**OXYGEN ISOTOPIC VARIATIONS IN THE INNER SOLAR SYSTEM  
1:30 p.m. Kachina Ballroom**

**Chair: J. Farquhar**

Clayton R. N. \* [Invited 30-Minute Overview]

*Oxygen Isotopic Compositions of the Terrestrial Planets*

Ireland T. R. \* Holden P. Norman M. Clarke J.

*Non-Linear Fractionation of Oxygen Isotopes Implanted in Lunar Metal Grains: Solar, Lunar or Terrestrial Origin?*

Young E. D. \*

*The Role of Water in Determining the Oxygen Isotopic Composition of Planets*

Jambon A. \*

*Isotopic Zoning in the Inner Solar System*

Franchi I. A. \* Greenwood R. C.

*Oxygen Isotopic Variation of the Terrestrial Planets*

Wiechert U. \* Halliday A. N. Palme H. Rumble D.

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Rahn T. \* Eiler J.

*Experimental Constraints on the Oxygen Isotope ( $^{18}\text{O}/^{16}\text{O}$ ) Fractionation in the Ice/Vapor and Adsorbate/Vapor Systems of  $\text{CO}_2$  at Conditions Relevant to the Surface of Mars*

Farquhar J. \*

*Exchange Between the Atmosphere and the Regolith of Mars: Discussion of Oxygen and Sulfur Isotope Evidence*

**Tuesday, July 20, 2004**

**POSTER SESSION**

**6:00 – 8:00 p.m. Tewa/Nambe Rooms**

Berlin J. Spilde M. Brearley A. J. Draper D. S. Dyar M. D.

*In Situ Determination of  $Fe^{3+}/Fe$  of Spinel by Electron Microprobe: An Evaluation of the Flank Method*

Kilinc A. I. Gerke T.

*Variation of  $K_d$  for Fe-Mg Exchange Between Olivine and Melt for Compositions Ranging from Alkaline Basalt to Rhyolite*

Libourel G. Marty B. Humbert F. Gayer E.

*Nitrogen Solubility in Basaltic Melt. Effects of Oxygen Fugacity, Melt Composition and Gas Speciation*

McKay G.

*The Europium Oxybarometer: Power and Pitfalls*

Rubie D. C. Gessmann C. Frost D. J.

*Solubility of Oxygen in Liquid Iron at High Pressure and Consequences for the Early Differentiation of Earth and Mars*

Shornikov S. I.

*Thermodynamic Study of Dissociation Processes of Molecular Oxygen in Vapor over Oxide Compounds*

Smith H. D. McKay C. P. Rainey F. Bebout B. Carpenter S.

*Oxygen Profile of a Thermo-Haliophilic Community in the Badwater Salt Flat*

Tachibana S. Hirai T. Goto K. Yamamoto S. Kirschvink J. L. Kopp R. E. Ohkouchi N.

Isozaki Y. Tada R. Tajika E. Kita N. T. Morishita Y.

*Mass-Independent Isotopic Fractionation of Sulfur from Sulfides in the Huronian Supergroup, Canada*

**Wednesday, July 21, 2004**

**REDOX VARIATIONS WITHIN THE INNER SOLAR SYSTEM  
8:30 a.m. Kachina Ballroom**

**Chair: M. Wadhwa**

Wadhwa M. \* [Invited 30-Minute Overview]

*New Advances in Understanding the Redox Conditions on Mars, Moon, and Asteroids*

Jones J. H. \*

*Redox Conditions on Small Bodies*

Mittlefehldt D. W. \*

*Graphite-FeO Reactions and the Size of the Ureilite Parent Body*

Delano J. W. \*

*Redox State of the Moon's Interior*

Karner J. M. \* Sutton S. R. Papike J. J. Shearer C. K. Jones J. H. Newville M.

*Determining the Oxygen Fugacity of Lunar Pyroclastic Glasses Using Vanadium  
Valence — An Update*

Shearer C. K. \* Papike J. J.

*Oxygen Fugacity of Lunar Basalts and the Lunar Mantle. Range of  $f_{O_2}$  and the Effectiveness  
of Oxybarometers*

Nicholis M. G. \* Rutherford M. J.

*Oxidation-Reduction Processes on the Moon: Experimental Verification of Graphite Oxidation  
in the Apollo 17 Orange Glasses*

Herd C. D. K. \*

*Oxygen in Martian Meteorites: A Review of Results from Mineral Equilibria Oxybarometers*

Foley C. N. \* Wadhwa M. Borg L. Janney P. E.

*Implications of Isotopic and Redox Heterogeneities in Silicate Reservoirs on Mars*

England C. \* Hrubes J. D.

*Molecular Oxygen Mixing Ratio and Its Seasonal Variability in the Martian Atmosphere*

King P. L. \*

*Determining the Partial Pressure of Oxygen ( $P_{O_2}$ ) in Solutions on Mars*

**12:00–1:30      Lunch**

**Wednesday, July 21, 2004**

**OXYGEN ISOTOPIC VARIATIONS WITHIN THE EARTH**

**1:30 p.m. Kachina Ballroom**

**Chair: R. E. Criss**

**Criss R. E. \* [Invited 30-Minute Overview]**

*Terrestrial Oxygen and Hydrogen Isotope Variations: Primordial Values, Systematics, Subsolidus Effects, Planetary Comparisons, and the Role of Water*

**Ferguson K. M \* Gregory R. T.**

*Oxygen and Hydrogen Isotope Systematics of Atmospheric Water Vapor and Meteoric Waters: Evidence from North Texas*

**Gregory R. T. \***

*Hydrothermal Systems on Terrestrial Planets: Lessons from Earth*

**Valley J. W. \***

*Crustal Evolution and Maturation on Earth: Oxygen Isotope Evidence*

**Wiechert U. \***

*The Oxygen Isotope Composition of the Moon: Implications for Planet Formation*

**Thursday, July 22, 2004**

**GEOPHYSICAL CONSEQUENCES OF REDOX STATE  
8:30 a.m. Kachina Ballroom**

**Chair: S. J. Mackwell**

Kohlstedt D. L. \* Hier-Majumder S. Mackwell S. J. [Invited 30-Minute Overview]  
*The Influence of Oxygen Environment on Kinetic Properties of Silicate Rocks and Minerals*

Bystricky M. \* Kunze K.  
*The Effect of Oxygen Fugacity on Large-Strain Deformation and Recrystallisation of Olivine*

Tyburczy J. \*  
*Electrical Conductivity, Oxygen Fugacity, and Mantle Materials*

Constable S. \* Roberts J. J. Duba A.  
*The Effect of Oxygen Fugacity on Electrical Conduction of Olivine and Implications for Earth's Mantle*

Gaillard F. \* Schmidt B. C. MacCammon C. A. Pichavant M. Scaillet B. Mackwell S. J.  
*Redox Exchanges in Hydrous Magma*

Cooper R. F. \*  
*Redox Chemical Diffusion in Silicate Melts: The Impact of the "Semiconductor Condition"*

Mackwell S. J. \* Bystricky M.  
*The Effect of Oxygen Fugacity on Interdiffusion of Iron and Magnesium in Magnesiowüstite*

**12:00 Meeting Adjourns for the Day**

**Friday, July 23, 2004**

**EARLY ACCRETION/CORE FORMATION**

**8:30 a.m. Kachina Ballroom**

**Chair: H. St. C. O'Neill**

O'Neill H. St. C. \* [Invited 30-Minute Overview]  
*Oxygen and Core Formation in the Earth*

Agee C. B. \*  
*Experimental Constraints on Oxygen and Other Light Element Partitioning During Planetary Core Formation*

Drake M. J. \* Stimpfl M. Laurretta D. S.  
*How did the Terrestrial Planets Acquire Their Water?*

Chabot N. L. \* Draper D. S. Agee C. B.  
*Core Formation in the Earth: Constraints from Ni and Co*

Cottrell E. \* Walker D.  
*Ultra-High Temperature Effects in Earth's Magma Ocean: Pt and W Partitioning*

Rose L. A. \* Brennan J. M.  
*Testing the Magma Ocean Hypothesis Using Metal-Silicate Partitioning of Te, Se and S*

Rushmer T. \* Petford N.  
*Metallic Liquid Segregation in Planetesimals*

**Friday, July 23, 2004**

**REDOX VARIATION IN THE EARTH  
10:30 a.m. Kachina Ballroom**

**Chair: C. D. K. Herd**

Herd C. D. K. \* [Invited 30-Minute Overview]  
*The Oxidation State of the Earth's Upper Mantle*

Haggerty S. E. \*  
*Iron Titanium Oxides and What They Tell Us*

Kress V. C. \*  
*Redox Evolution of Magmatic Systems*

Rutherford M. J. \*  
*Volatiles in Magmas*

Li Z. \* Lee CT. A.  
*The Constancy of Upper Mantle  $f_{O_2}$  Through Time Inferred from V/Sc Ratios in Basalts: Implications for the Rise in Atmospheric  $O_2$*

**12:00–1:30      Lunch**



**Friday, July 23, 2004**

**EVOLUTION OF THE HYDROSPHERE-ATMOSPHERE-BIOSPHERE  
1:30 p.m. Kachina Ballroom**

**Chair: A. A. Pavlov**

Kasting J. F. • [Invited 30-Minute Overview]  
*Mantle Redox Evolution and the Rise of Atmospheric O<sub>2</sub>*

Delano J. W. •  
*Variation in Mantle Redox State over Time*

Thiemens M. H. •  
*Mass Independent Isotopes and Applications to Planetary Atmospheres*

Lyons J. R. •  
*Oxygen Isotope Anomalies in the Atmospheres of Earth and Mars*

Pavlov A. A. • Mills M. J. Toon O. B.  
*How Well do Sulfur Isotopes Constrain Oxygen Abundance in the Ancient Atmospheres?*

Ono S. • Wing B. Eigenbrode J. Rumble D. Farquhar J.  
*Geologic Record of the Atmospheric Sulfur Chemistry Before the Oxygenation of the Early Earth's Atmosphere*

**EXPERIMENTAL CONSTRAINTS ON OXYGEN AND OTHER LIGHT ELEMENT PARTITIONING DURING PLANETARY CORE FORMATION.** C. B. Agee, Institute of Meteoritics and Department of Earth and Planetary Sciences, University of New Mexico, Albuquerque NM 87131, agee@unm.edu.

**Introduction:** The nature of the light element content of the Earth's molten outer core has been actively debated since Birch [1] first proposed that some mix of light elements such as O, S, and Si could account for the apparent 10% density deficit there. Over the past several years numerous high-pressure experimental studies have placed important constraints on the physics and chemistry of planetary core formation. Based on siderophile element partitioning studies [2-4] core formation for the Earth appears to have occurred within a deep magma ocean. Thus the effects of pressure and temperature are important factors to consider in modelling the fate of light elements during core-mantle segregation. Here I review our current knowledge of oxygen, sulfur, and silicon partitioning between Fe-metal and silicate at extreme conditions, and the constraints these data place on light element behavior during planetary core formation.

**Oxygen:** Kato and Ringwood [5] performed some of the first exploratory partitioning experiments and suggested that a pressure effect would cause sufficient oxygen to dissolve into iron metal at the Earth's core-mantle boundary to account for the density deficit. More recent work by O'Neill et al. [6] and Rubie et al. [7] contradict Kato and Ringwood, showing that pressure actually decreases the solubility of oxygen with pressure. Li and Agee [8] and Rubie et al. [7] performed isobaric experiments up to 2673K and observed a strong positive temperature effect on  $D_{\text{O}}$  metal/silicate at constant  $f\text{O}_2$ . This result led Rubie et al. to propose that terrestrial planets of different size can end up with dramatically different core mass fractions and mantle iron oxide compositions – even if they formed from the same solar nebula or chondritic material. For example, this may be possible if the Earth's magma ocean was under higher pressure and thus hotter during core formation, while Mars' magma ocean had only modest pressures and temperatures.

**Sulfur:** Li and Agee [8] examined the effects of pressure and temperature on sulfur partitioning between molten iron-alloy and molten silicate in carbonaceous and ordinary chondrite starting materials up to 20 GPa and 2673K. Here pressure has a dramatic positive effect on  $D_{\text{S}}$  metal/silicate increasing from 74 to 533 over the pressure range 2-20 GPa at constant  $T=2273\text{K}$ . Temperature, on the other hand, decreases  $D_{\text{S}}$ . For example, over the range 2073-2623K, under isobaric conditions at 10 GPa,  $D_{\text{S}}$  decreases from 302 to 81. Even though the strong pressure effect is dampened by an offsetting negative temperature effect,  $D_{\text{S}}$  is

expected to remain significantly greater than unity at all conditions of planetary core formation. Thus, sulfur may be one of the dominant light elements in the core if a sufficient quantity of it was sequestered in the Earth during accretion. Interestingly, the partitioning data indicate that the sulfur content of the upper mantle (250 ppm) is too high to have equilibrated with a molten outer core containing 2-10 wt% sulfur. Mass balance requires that additional sulfur be added to the upper mantle from other sources, possibly as part of a 0.2-0.6% Earth-mass late veneer.

**Silicon:** Li and Agee [8] found that temperature and pressure no have detectable effects on the partitioning of Si between Fe-metal and silicate in chondritic starting materials at  $f\text{O}_2$  ranging from the iron-wuestite (IW) buffer to 2 log units below IW. Under highly reducing conditions,  $D_{\text{Si}}$  has been shown to increase significantly [9,10], however for Si to be the dominant light element in the core would require an  $f\text{O}_2$  of approximately log  $\text{IW}-4$  to  $-6$ , much lower than is suggested by the Earth's core mass and FeO content of mantle xenoliths.

**References:** [1] Birch, F. J. *Geophys. Res.* 69, 4377-4388 (1964). [2] Li, J. & Agee, C.B. *Nature* 381, 686-689 (1996). [3] Li, J. & Agee, C.B. *Geochim. Cosmochim. Acta.* 65, 1821-1832 (2001). [4] Chabot, N.L. & Agee, C.B. *Geochim. Cosmochim. Acta* 67, 2077-2091 (2003). [5] Kato, T. & Ringwood, A.E. *Phys. Chem. Minerals* 16, 524-538 (1989). [6] O'Neill, H.S.C., Canil, D. & Rubie, D.C. *J. Geophys. Res.* 103, 12,239-12,260 (1998). [7] Rubie, D.C., Gessmann, C.K. & Frost, D.J. *Nature* in press (2004). [8] Li, J. & Agee, C.B. *Geophys. Res. Lett.* 28, 81-84 (2001). [9] Kilburn, M.R. & Wood, B.J. *Earth Planet. Sci.* 152, 139-148 (1997). [10] Gessmann, C.K. & Rubie D.C. *Geochim. Cosmochim. Acta* 62, 867-882, (1998).

**IN SITU DETERMINATION OF  $\text{Fe}^{3+}/\Sigma\text{Fe}$  OF SPINELS BY ELECTRON MICROPROBE: AN EVALUATION OF THE FLANK METHOD.** J. Berlin<sup>1</sup>, M. Spilde<sup>2</sup>, A. J. Brearley<sup>1</sup>, D. S. Draper<sup>2</sup> & M. D. Dyar<sup>3</sup>. <sup>1</sup>Department of Earth & Planetary Sciences, University of New Mexico, Albuquerque, NM 87131, U.S.A., <sup>2</sup>Institute of Meteoritics, University of New Mexico, Albuquerque, NM 87131, U.S.A., <sup>3</sup>Department of Earth and Environment, Mount Holyoke College, South Hadley, MA 01075, U.S.A., E-mail: [jberlin@unm.edu](mailto:jberlin@unm.edu)

**Introduction:** In the past decade, progress has been made in the *in situ* determination of  $\text{Fe}^{3+}/\Sigma\text{Fe}$  ratios of minerals (which can be used to infer oxygen fugacity,  $f\text{O}_2$ ) with techniques such as TEM-EELS, Mössbauer milliprobe, and microXanes [1-3]. In addition, electron microprobes can measure the intensity change and shift of the L lines with the oxidation state of iron [4-7]. We are currently investigating potential applications of the Flank method [4-6] to geologic problems. Our goal is to evaluate whether the Flank method can be used to detect variation of  $\text{Fe}^{3+}/\Sigma\text{Fe}$  (and hence  $f\text{O}_2$ ) in spinel grains from terrestrial mantle xenoliths.

**Technique:** The Flank method [4-6] uses the differences between Fe L line spectra of Fe oxides with varying oxidation states (wüstite, magnetite, hematite) which are most pronounced on the low energy flank of the Fe  $\text{L}\beta$  line and on the high energy flank of the Fe  $\text{L}\alpha$  line. When X-ray intensities are determined at fixed wavelengths on the flanks of the  $\text{L}\alpha$  and  $\text{L}\beta$  peaks, the  $\text{L}\beta/\text{L}\alpha$  intensity ratios are inversely correlated with the  $\text{Fe}^{3+}/\Sigma\text{Fe}$  ratios for the three pure Fe oxides. For these phases, an error as small as 0.02 for the  $\text{Fe}^{3+}/\Sigma\text{Fe}$  ratio is obtained [4]. However, for more complex minerals, matrix effects (chemical bonding and composition) affect the  $\text{L}\beta/\text{L}\alpha$  ratio dramatically. To account for these matrix effects and before the method can be applied to minerals with unknown  $\text{Fe}^{3+}/\Sigma\text{Fe}$  ratios, working curves need to be established as was done for synthetic garnets by Höfer & Brey [6].

**Samples:** In order to investigate if a Flank-method calibration curve for spinels can be established, we are using samples with  $\text{Fe}^{3+}/\Sigma\text{Fe}$  ratios that have been determined previously by Mössbauer spectroscopy on bulk spinel separates. These include spinels from the Simcoe volcano, Washington [8], Cima and Dish Hill, California as well as from Harrat al Kishb and Harrat Hutaymah, Saudi Arabia. The Simcoe spinels have similar bulk compositions ( $\text{Mg}\# = 69.0\text{--}72.4$ ,  $\text{Cr}/\text{Cr}+\text{Al} = 31.9\text{--}34.5$ ) and range in  $\text{Fe}^{3+}/\Sigma\text{Fe}$  from 27 to 38. The other spinels show a wide range of compositions ( $\text{Mg}\# = 70.0\text{--}78.6$ ,  $\text{Cr}/\text{Cr}+\text{Al} = 9.8\text{--}32.2$ ) and have  $\text{Fe}^{3+}/\Sigma\text{Fe}$  from 12 to 37.

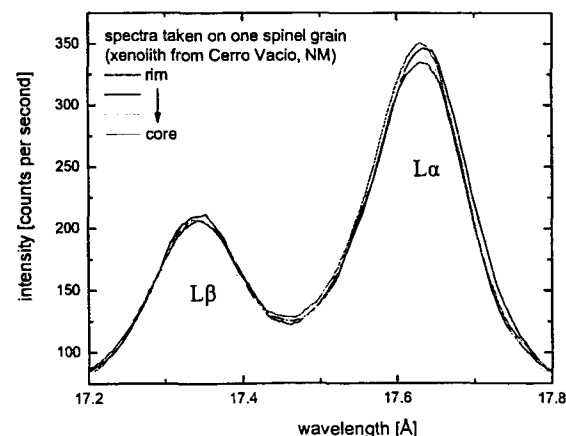
We are also analyzing xenolith samples from the Puerco Necks, New Mexico, for which Mössbauer data have not been obtained yet. Spinel in these samples are especially likely to have variations of  $\text{Fe}^{3+}/\Sigma\text{Fe}$  on the microscopic scale as they show compositional zoning

in addition to exhibiting a wide range of colors (brown, black, green, and purple).

**Preliminary results:** The calibration of the Flank method for spinels is complicated by many factors such as the huge range of compositional, structural, and bonding effects which can change the shape of the Fe L lines. In addition, instrumental parameters such as spectrometer reproducibility [5] and stability of the beam current during the measurements need to be monitored carefully. Keeping the beam current constant ( $50.0 \pm 0.2$  nA), we have found significant variations in the shapes of Fe L spectra taken on single spinel grains of Puerco neck xenoliths (Fig. 1). However, these variations are not systematic in a way that would imply core-to-rim zoning in  $\text{Fe}^{3+}/\Sigma\text{Fe}$  and thus  $f\text{O}_2$ .

**Acknowledgements:** We are grateful to A. Brandon and J. Selverstone, who are providing samples for this study.

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**Fig. 1:** Fe L emission spectra taken on one spinel grain in a xenolith sample from Cerro Vacio, NM (10 keV, 50 nA, TAPJ crystal). The spectra are smoothed.

**THE EFFECT OF OXYGEN FUGACITY ON LARGE-STRAIN DEFORMATION AND RECRYSTALLIZATION OF OLIVINE.** M. Bystricky and K. Kunze. Geologisches Institut, ETH Zürich, Sonneggstrasse 5, CH-8092 Zürich, Switzerland.

**Abstract:**

The rheological properties of olivine, the most abundant phase in the Earth upper mantle, are likely to govern mantle dynamics. In particular, the development of crystallographic preferred orientations (CPOs) in olivine during deformation and recrystallization gives rise to seismic anisotropy in the mantle. Recent experimental studies have shown that different CPOs develop at large strains for dry olivine [1-2], wet olivine [3] and olivine with melt [4]. In this study, we have focused on the effect of oxygen fugacity on the deformation and recrystallization of dry olivine.

Large-strain deformation experiments were performed on hot-pressed polycrystalline olivine aggregates under conditions (temperature, pressure, strain rate and grain size) favoring dislocation creep. Cylindrical samples were deformed in torsion in a gas-medium apparatus at 1200-1300°C, a confining pressure of 300 MPa and constant twist rates corresponding to constant shear strain rates of  $5 \cdot 10^{-5}$  to  $3 \cdot 10^{-4} \text{ s}^{-1}$  at the samples' outer diameters. The oxygen fugacity was controlled by placing the samples in an iron or a nickel sleeve, yielding oxygen fugacities near the iron-iron wüstite (Fe/FeO) or the nickel-nickel oxide (Ni/NiO) phase boundaries, respectively. Simple shear microstructures were observed by light microscopy and CPOs were analysed by orientation mapping using electron backscatter diffraction.

The strength of dry polycrystalline olivine is weakly dependent on oxygen fugacity. At low strain, peak stress values (at both Ni/NiO and Fe/FeO) are very consistent with previous rheological data on dislocation creep of olivine obtained in coaxial experiments under dry conditions [5-6]. Microstructures show evidence for dislocation creep and recovery in the form of deformation lamellae and subgrains. A typical deformation texture with [100] axes oblique to the shear direction is present at shear strains of  $\sim 0.5$ .

After the initial peak stress, significant weakening occurs with increasing shear strain ( $\gamma \sim 0.3$ -3). Weakening becomes less important at larger strains and stress seems to approach a steady value at shear strains of  $\gamma \sim 6$ -8. The total weakening at large strains is approximately 20-40%. The determination of stress exponents of about 3-3.5 at various finite strains and of strong CPOs in all deformed samples suggest that dis-

location creep processes remain dominant throughout the experiments.

Microstructural observations of samples deformed at Fe/FeO and 1200-1250°C indicate continuous dynamic recrystallization mainly by subgrain rotation and some grain boundary migration. Recrystallization is accompanied by important grain refinement and leads to strongly foliated microstructures. With increasing temperature, grain boundaries become much more mobile. At 1300°C recrystallization occurs mainly by grain boundary migration, producing microstructures with a less pronounced foliation. At all temperatures, a strong recrystallization CPO in highly deformed samples is characterized by alignment of [100] in the shear direction and girdles of [010] and [001] approximately normal to that direction. This texture is interpreted as due to dislocation glide on several  $\{0kl\}[100]$  slip systems, including activation of (010)[100].

At Ni/NiO, recrystallization is more efficient and seems to be dominated by grain boundary migration. Straight and parallel grain boundaries are often aligned across several grains, suggesting some contribution of grain boundary sliding at large strains, possibly assisted by diffusion processes. A strong CPO with [100] aligned in the shear direction and a [010] point maximum perpendicular to the shear plane suggest dislocation creep primarily on the (010)[100] slip system.

Our study shows that during large strain deformation and recrystallization of dry olivine in the dislocation creep regime, more oxidizing conditions promote diffusion processes and grain boundary sliding. Although the presence of a strong CPO suggests that dislocation creep remains active at large strains, grain boundary sliding processes may accommodate some of the strain leading to a de-emphasis of stronger slip systems in olivine in favor of dominant slip on the single (010)[100] slip system.

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**PLAGIOCLASE-LIQUID TRACE ELEMENT OXYGEN BAROMETRY AND OXYGEN BEHAVIOUR IN CLOSED AND OPEN SYSTEM MAGMATIC PROCESSES.** Dante Canil<sup>1</sup> and James Thom<sup>2</sup> <sup>1</sup>School of Earth and Ocean Sciences, University of Victoria, Victoria, B.C., Canada, dcanil@uvic.ca <sup>2</sup>Department of Earth and Ocean Sciences, University of British Columbia, Vancouver, B.C..

**Introduction:** There are several measurements of the oxygen fugacity recorded by magmas, and related concern about the behaviour of oxygen in magmas. Do magmas exchange oxygen in an open process through homogeneous equilibria, or do they remain closed systems along their liquid line of descent? Evidence for mixing of several magma batches in many magma types suggests truly open systems, and many oxygen barometers record crystallization along or parallel to 'buffers' such that the magma must exchange oxygen or 'breathe' by interaction with a separate redox reservoir, likely sulfur [1].

In this study, we explore the use of trace element signatures in plagioclase as an indicator of the oxygen fugacity recorded by magmas with multiple histories, or by extraterrestrial samples. Plagioclase is a ubiquitous mineral in magmas ranging in composition from basalt to rhyolite, and often shows a detailed record of the magma batches into which it has been mixed and recycled. We experimentally calibrate the partition of redox sensitive elements (V, Mn) into plagioclase with a view to using concentration profiles for these elements to infer conditions of oxygen fugacity during crystallization, mixing, resorption and recycling, or as an empirical oxygen barometer in many terrestrial and extraterrestrial samples for which no other traditional methods can be employed.

**Methods:** Experiments were performed at 100 kPa in synthetic (Di-Ab-An) and natural systems (MORB, alkali basalt) in a vertical tube furnace, with  $fO_2$  fixed by CO – CO<sub>2</sub> gas mixing. Natural basalts were crystallized between 1200 and 1150°C at  $fO_2$  conditions of about one to four log units below the nickel-bunsenite (NNO) buffer (NNO-1 to NNO-4). Cooling histories were used to produce large plagioclase grains (300 microns) and glass for analysis by laser ablation inductively coupled plasma mass spectrometry (LA ICP MS). Charges were mounted on Re ribbon or pre-saturated Pt wire loops, to avoid Fe loss. Some experiments were 'reversed' by approaching final conditions from both low and high  $fO_2$ .

**Results:** Over an increase in  $fO_2$  of only 2 log units (NNO-3.5 to NNO-1.5), Mn and V concentrations in plagioclase decrease from 600 to 30 ppm, and from 150 to 5 ppm, respectively. Liquid composition is constant in Mn (~ 1300 ppm) and V (~ 250 ppm) in all

experiments. The resultant partition coefficients,  $DMn$  and  $DV$  (plag/liq) are similar and vary from ~ 0.4 to ~0.02 between NNO-3.5 to NNO-1.5. The changes in  $DMn$  and  $DV$  with  $fO_2$  are thus dominated by substitution into the crystal. The  $D(plag/liq)$  for Ga, REE, Mg, Ca, Ba, and Sr were also determined by LA ICP MS in the same experiments. Onuma diagrams (logD element vs. ionic radius) show that Mn enters plagioclase principally as  $Mn^{2+}$ . The case is less clear for  $V^{2+}$ . The large changes in  $D$  plag/liq for these elements with increasing oxygen fugacity are due to less  $Mn^{2+}$  (or  $V^{2+}$ ) available in the liquid for substitution into plagioclase.

We apply our partitioning data in a preliminary way to mid-Atlantic MORB and arc basalts from the Kuriles and from Mt. Adams, Washington. We obtain  $fO_2$ 's of NNO-2.5 and NNO-1, respectively, consistent with previous measurements and with 'conventional wisdom'. Current applications in progress are to unravel the redox history recorded by zoned plagioclase in erupted rocks from mid-ocean ridges, Mt. St. Helens, Washington, and Mt. Meager, British Columbia. Coupled with these experimental results, the growing use of trace element microanalysis in petrology should provide further constraints on the detailed behaviour of oxygen during the crystallization, mixing and eruption of any terrestrial or extraterrestrial magma having plagioclase on its liquidus.

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**CORE FORMATION IN THE EARTH: CONSTRAINTS FROM NI AND CO.** N. L. Chabot<sup>1</sup>, D. S. Draper<sup>2</sup>, and C. B. Agee<sup>2</sup>, <sup>1</sup>Dept. of Geology, 112 A. W. Smith Bldg., Case Western Reserve University, Cleveland, OH, 44106-7216. nlc9@po.cwru.edu. <sup>2</sup>Institute of Meteoritics, Department of Earth and Planetary Sciences, University of New Mexico, Albuquerque, NM, 87131-1126.

Due to their metal-loving nature, Ni and Co were strongly partitioned into the metallic core and were left depleted in the silicate mantle during core formation in the Earth. Based on experimental liquid metal-liquid silicate partition coefficients ( $D$ ), studies have suggested that core formation in an early magma ocean can explain the observed mantle depletions of Ni and Co [1-5]. However, the conditions proposed by the magma ocean models have ranged from pressures of 24 to 59 GPa and temperatures of 2200 to < 4000 K. Furthermore, the proposed magma ocean oxygen fugacities have differed by nearly two orders of magnitude, from 0.4 to 2.2 log units below the iron-wüstite buffer ( $\Delta IW = -0.4$  to  $-2.2$ ).

Chabot and Agee [6] noted that the different models predicted contradictory behaviors for  $D(\text{Ni})$  and  $D(\text{Co})$  as a function of temperature. With the hope of resolving the discrepancies between the magma ocean models, we conducted a systematic experimental study to constrain the effects of temperature on  $D(\text{Ni})$  and  $D(\text{Co})$ . Our preliminary multi-anvil experimental results are shown in Fig. 1.

Combining our temperature results with the well-determined effects of pressure from previous studies [e.g. 1, 5] and treating Ni and Co as divalent [e.g. 7], we have parameterized  $D(\text{Ni})$  and  $D(\text{Co})$  as functions of pressure, temperature, and oxygen fugacity, using a mathematical form similar to previous work [2-5]. For compositions appropriate to the Earth's core, the effects of S and C on  $D(\text{Ni})$  and  $D(\text{Co})$  are small [6, 8], as are the effects from silicate composition [9].

Using our parameterizations, we can get pressure, temperature, and oxygen fugacity solutions where  $D(\text{Ni})$  and  $D(\text{Co})$  are both within a factor of two of the partition coefficients needed to explain the mantle depletions by core formation in a magma ocean. Figure 2 shows the solution spaces for two different oxygen fugacities proposed by the magma ocean models. Surprisingly, despite very different predicted effects of temperature by the models, all of the previous models fall in one of our determined solution spaces. Thus, our work shows the proposed conditions are all mathematically possible. However, if the FeO content of the mantle is used as an additional constraint, the oxygen fugacity suggested by core-mantle equilibrium is about  $-2.2 \Delta IW$ , supporting core formation in a magma ocean at 40 to 60 GPa and a temperature > 2500 K.

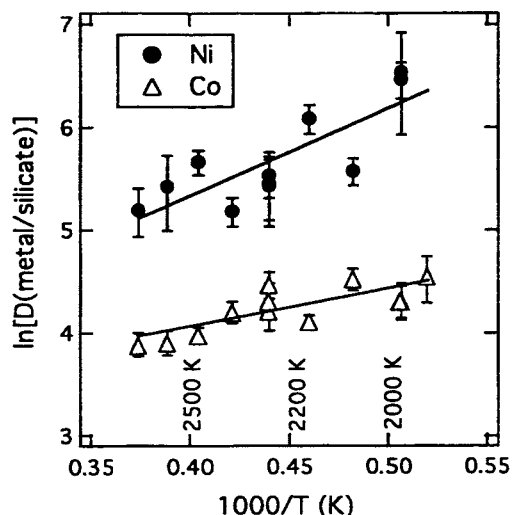


Fig. 1. Experimental data at 7 GPa with  $2\sigma$  errors, corrected to a common oxygen fugacity of  $-1.5 \Delta IW$ .

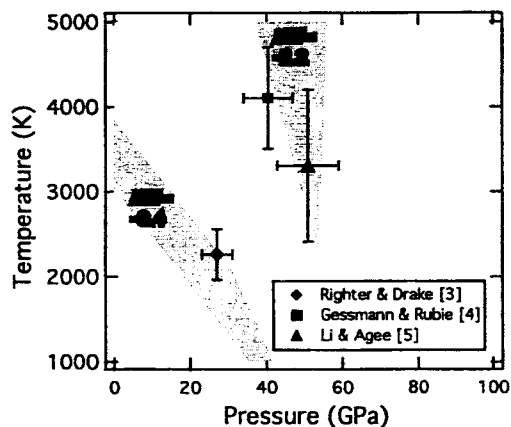


Fig. 2. The two shaded areas show the solution spaces for oxygen fugacities of  $-0.4$  and  $-2.2 \Delta IW$ , where our parameterized  $D(\text{Ni})$  and  $D(\text{Co})$  both fall within a factor of two of the needed values.

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**OXYGEN ISOTOPIC COMPOSITIONS OF THE TERRESTRIAL PLANETS.** Robert. N. Clayton, Enrico Fermi Institute, University of Chicago, Chicago, IL 60637, USA. r-clayton@uchicago.edu

Mechanisms that may account for oxygen isotope heterogeneity in meteorites on the microscopic scale do not seem adequate for explaining the similarities and differences in isotopic composition on a planetary scale. In chondrites, most of the isotopic variability can be attributed to photochemical enrichment of the two rare heavy isotopes with respect to the  $^{16}\text{O}$ -rich solar composition [1]. In the CO, CM, CI, and CR chondrites, an additional low-temperature aqueous alteration leads to mass-dependent further enrichment of the heavy isotopes.

If the proposed origin of the isotopic variation in chondrites is correct, then only a small fraction, represented primarily in CAIs, has the solar oxygen isotopic composition, and all other meteoritic components must have undergone photochemical processing. In addition, since the bulk isotopic compositions of the terrestrial planets and of the achondrite parent bodies are similar to those of chondrites, they too must be made of photochemically enriched matter. The photochemical reactions produce a non-equilibrium assemblage of gases, probably leading to a non-equilibrium assemblage of solids, particularly with respect to their oxidation state. These issues emphasize the importance of the measurement of oxygen isotopes in the Genesis solar wind mission.

Within the Earth, oxygen isotope variations are due almost entirely to mass-dependent fractionation effects, giving a line of slope 0.52 on the three-isotope plot. The average crustal composition is 3–4‰ higher in  $\delta^{18}\text{O}$  than the upper mantle. This difference is too large to be due to igneous fractionation effects alone, and reflects the larger, low-temperature iso-

tope fractionation associated with aqueous weathering reactions at the Earth's surface. Similar effects are not observed in the intraplanetary isotopic variations in the Moon or in the parent bodies of the HED and SNC meteorites.

The bulk oxygen isotopic compositions of Earth and Mars (assumed to be the SNC parent body) cannot be accounted for by any mixture of two components, such as those proposed by Ringwood [2] and Wänke [3]. In principle, three-component mixtures of ordinary chondrites, CI, and CV chondrites can match the planetary isotopic compositions, but are inconsistent with chemical compositions. An additional unexplained observation is the exact coincidence in oxygen isotopic composition between Earth and Moon. The correspondence of isotopic composition between the Earth and the enstatite chondrites has been taken by some to have direct genetic significance [4]. In all models using primitive chondrites as building blocks for the terrestrial planets, there is a necessity to remove a major fraction of the moderately volatile elements (alkalies, S, etc.), without altering their isotopic compositions [5].

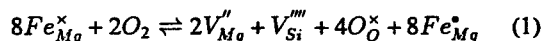
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**THE EFFECT OF OXYGEN FUGACITY ON ELECTRICAL CONDUCTION IN OLIVINE AND IMPLICATIONS FOR EARTH'S MANTLE.** S. Constable<sup>1</sup>, J.J. Roberts<sup>2</sup>, and A. Duba<sup>3</sup>. <sup>1</sup>Scripps Institution of Oceanography, La Jolla, CA 92093-0225, sconstable@ucsd.edu. <sup>2</sup>Lawrence Livermore National Laboratory, Livermore, CA 94551, roberts17@llnl.gov. <sup>3</sup>American Museum of Natural History, New York, NY 10024-5192, duba@amnh.org.

**Abstract:** Because electrical conductivity is exponentially dependent on temperature and also a function of composition and phase, studies of mantle conductivity have long held the promise of providing information on the thermal and compositional state of Earth's mantle. Two techniques for probing deep conductivity exist; the magnetotelluric (MT) method of recording surface magnetic and electric fields, and the geomagnetic depth sounding (GDS) method of separating externally generated and internally induced magnetic fields from vector magnetometer records. The GDS method has recently gained momentum from the application of magnetic satellite data, which provide a global coverage not possible using land-based observatories alone [1].

The bridge between these field studies and the internal constitution of Earth is provided by laboratory measurements of Earth materials as a function of temperature, composition, and pressure. Oxygen fugacity  $f_{O_2}$  plays many important roles in this enterprise. First and foremost,  $f_{O_2}$  must be controlled sufficiently to keep the sample within its stability field, or irreversible changes in composition and conductivity occur [2]. Secondly, electrical conductivity of olivine, and presumably other mantle materials in which iron influences conductivity and stoichiometry, depends on  $f_{O_2}$  and the oxidation state of the mineral. Thirdly,  $f_{O_2}$  can be used as a laboratory tool for probing the behavior of defects in mantle minerals.

We have studied the effect of oxygen on the electrical properties of olivine,  $(Mg_{0.9}Fe_{0.1})_2SiO_4$ , the dominant mineral of Earth's upper mantle, in an effort to quantitatively describe conduction mechanism, charge mobility, and defect concentration. The working model for the relationship between the major defect populations and  $f_{O_2}$  is described by



[3,4] with magnesium vacancies  $V_{Mg}''$  and polarons (holes localized on  $Fe_{Mg}^{\bullet}$ ) both candidates for dominant conduction defects. Room pressure electrical conductivity as a function of temperature and  $f_{O_2}$  demonstrates an increase in conductivity with both parameters, representing the combined effects of increased mobility, representing the concentration, and shifting conduction mechanism. The addition of thermopower measurements, in which the electric field generated by a temperature gradient is measured, allows one to separate the mobility term from concentration. A mathematical model describing conductivity and thermopower as a function of mobility, concentration, and defect type is inverted to obtain separate estimates of the defect concentrations  $[V_{Mg}'']$  and  $[Fe_{Mg}^{\bullet}]$  as well as their mobilities [5]. The contribution of these defects to electrical conduction in olivine, and thus presumably the mantle, varies by nearly an order of magnitude as  $f_{O_2}$  spans the stability field.

In an independent experiment, the exponential change in conductivity after an abrupt change in  $f_{O_2}$  external to the sample can be used to estimate the diffusivity, and thus mobility, of defects responsible for chemical re-equilibration [6]. Again, an extensive data set of relaxation times as a function of  $f_{O_2}$  and temperature was modeled to extract mobility as a function of temperature for multiple defect species. The mobilities of the two species required by the re-equilibration data agrees extremely well with the mobilities for  $V_{Mg}''$  and  $Fe_{Mg}^{\bullet}$  derived from the thermopower modeling, suggesting that these conductive species are also responsible for the rate of the defect reaction (1). The agreement (shown in Fig. 1) between the two different methods (thermopower modeling and  $f_{O_2}$  re-equilibration) carried out on two different samples (San Quintin dunite and Mt. Pomdon lherzolite) suggests that the mobilities derived for these defects are reliable.

Although many uncertainties and unconstrained variables remain in our efforts to characterize mantle conductivity (for example, the role of hydrogen/water in conduction), it is clear that the effect of oxygen cannot be ignored when interpreting field measurements using laboratory data sets.

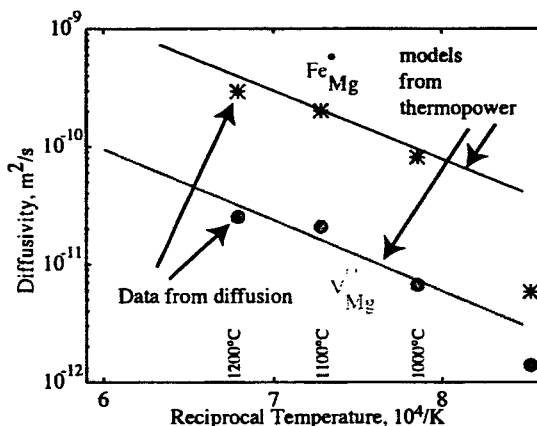


Figure 1: Diffusivities for  $V_{Mg}''$  and  $Fe_{Mg}^{\bullet}$  derived from thermopower mobilities (lines) and  $f_{O_2}$  re-equilibration (symbols) as a function of temperature.

#### References:

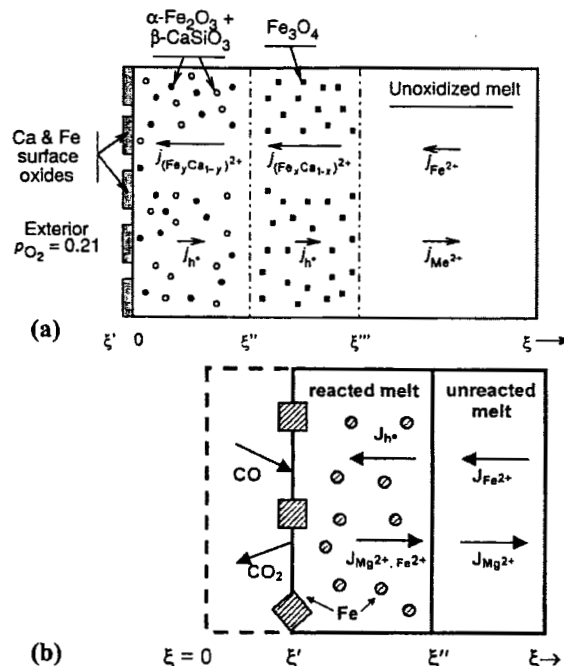
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**REDOX CHEMICAL DIFFUSION IN SILICATE MELTS: THE IMPACT OF THE "SEMICONDUCTOR CONDITION."** Reid F. Cooper, Department of Geological Sciences, Brown University, Providence, RI 02012-1846 USA (Reid\_Cooper@Brown.edu).

**Introduction:** Transition-metal-cation redox experiments designed to characterize the rate of oxygen-species diffusion in silicate melts reveal a startling result: for melts of similar polymerization, chemical diffusion seems to occur some  $10^2$ – $10^3$  times faster than that seen for  $^{18}\text{O}$  in tracer diffusion experiments [1–3]. The primary reason for the discrepancy is that, in many cases, the chemical diffusion producing the valence-state change of transition-metal cations does not involve diffusion of an oxygen species at all, but rather is wrought by the diffusion of network-modifying cations whose motion is decoupled from that of other ions by the high transport coefficient of electronic defects, i.e., electron holes ( $h^*$ ) and/or electrons in the conduction band ( $e^-$ )—a situation known as the “semiconductor condition” in chemical kinetics [4]. Cation-diffusion-effected redox reactions, in both melts and minerals, create reaction morphologies with implications, e.g., for the perceived chemistry of planetary surfaces and for the structures of metal-bearing chondrules.

**Oxidation of basaltic magmas:** Ion backscattering spectrometry was used to prove unequivocally (i.e., the reaction morphology is unique) that the physical process of oxidation of a basaltic liquid occurs, for anhydrous conditions, according to the dynamic shown in Fig. 1a [5]. When the external oxygen fugacity ( $f_{\text{O}_2}$ ) exceeds the magnetite-hematite (MH) buffer, two internal reaction fronts move into the melt:  $\xi'''$  is the location where the local  $f_{\text{O}_2}$  finally sees the melt go subliquidus, and magnetite nucleates;  $\xi''$  is the MH buffer, where the magnetite formed in the first (crystallization) reaction is converted to hematite. The process is accomplished by the flux ( $j_i$ ) of network-modifier  $\text{Fe}^{2+}$  and  $\text{Ca}^{2+}$  to the free surface, where they form thin-film oxides that coat the surface. The cation flux is charge-compensated by a counterflux of  $h^*$ . For  $f_{\text{O}_2}$  conditions lower than MH but sufficiently high to intersect the liquidus, only the single reaction front  $\xi'''$  moved into the melt, and very little  $\text{Ca}^{2+}$  is mobilized; thus  $x$  in the figure approaches unity and  $y \ll x$ . The thin-film oxide is seen naturally as the multicolored specular patina on fresh basalt flows [e.g., 6], the color variation being a function of the film thickness. Reflectance spectroscopy on these surfaces clearly would reveal a  $\text{Fe}^{2+,3+}$  content exceeding greatly that of the bulk magma. The cation-diffusion-dominated oxidation response was proven to occur for  $\text{Fe}^{2+,3+}$  concentrations as low as 0.04 at% [7].



**Figure 1.** Redox dynamics in  $\text{Fe}^{2+,3+}$ -bearing silicate melts. (a) Oxidation in a basaltic melt. (b) Reduction in an Fe-MAS melt. Cation-diffusion-effected reactions are possible because of the flux of electron holes.

**Reduction of iron-oxide-bearing melts:** Experiments on  $\text{Fe}^{2+}$ -doped magnesium aluminosilicate (Fe-MAS) melts demonstrated the reduction dynamic depicted in Fig. 1b [8]: oxygen chemically ablates from the free surface and network-modifying cations diffuse inward, charge-compensated by a counterflux of  $h^*$ ; nm-scale crystals of  $\alpha\text{-Fe}$  nucleate at an internal front,  $\xi''$ . Dispersal of iron grains suggests that the melt structure includes percolation of network modifiers. Surface iron crystals are affected by vapor-phase transport of iron. Lowering the  $f_{\text{O}_2}$  further, via increase in  $\text{CO}$  content of environment, sees a mechanism change to one in which a carbon species diffuses inward.

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**ULTRA-HIGH TEMPERATURE EFFECTS IN EARTH'S MAGMA OCEAN: Pt and W PARTITIONING.**

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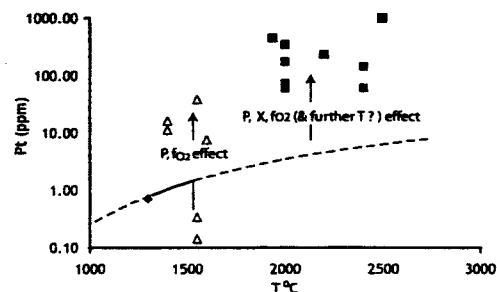
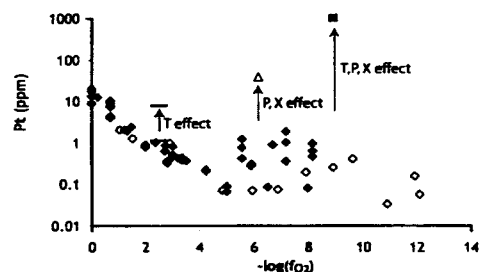
**Abstract:** New experiments to 2600°C (at 2 GPa, reducing conditions, at ~constant relative  $f_{O_2}$ ) demonstrate a very strong negative dependence of  $D_{Pt}^{met/sil}$ , and a weak negative dependence of  $D_W^{met/sil}$  on T. The Pt results reconcile mantle Pt abundances with the magma ocean model as suggested by [1], and also resolve the "nugget problem." The W results allow hotter magma oceans to be compatible with mantle W abundance than if  $D_W^{met/sil}$  had a positive T dependence.

**Methods:** Ca-doped LaCrO<sub>3</sub> cylinders insulate short graphite (C) heaters from BaCO<sub>3</sub> piston cylinder pressure media while Mo-wrapped MgO spacers at either end of the C heaters insulate the piston and complete the electrical circuit. Experiments remain stable for 1-10 hours at T 2000-2600°C. For Pt experiments, a C capsule holds a small Pt clipping at the base of non-convecting, initially Pt-free silicate [2]. We initially used C capsules for W-silicate experiments; however, this resulted in prolific growth of metal carbides that rapidly (< 4 min at T ≥ 2000°C) established new equilibria. C capsules were replaced with pure W capsules for experiments on W solubility.

**Results for Pt:** At temperatures in excess of 2000°C silicate melt dissolves tens to hundreds of ppm Pt by weight – levels analyzed by EMP. Rapid quench results in concentric textural zones: the outermost (in contact with the C) is completely free of the micronuggets which have plagued previous investigations [3-5]. Interior regions of the silicate, which cooled more slowly, formed nuggets; however, the measured Pt concentration in the charge is spatially invariant. In addition, nugget size correlates with quench rate and is independent of run time. These observations in concert with the precautions taken by [2] strongly suggest a quench origin for Pt micronuggets. We measure  $D_{Pt}^{met/sil} \sim 10^3$ , 4-12 orders of magnitude lower than extrapolations from high  $f_{O_2}$ , 1 bar experiments at ≤ 1550°C [3-6] but consistent with measured Pt concentrations from [7], though our interpretations differ.

**Results for W:** Between 1450 and 2400°C in W capsules, holding silicate melt composition and relative  $f_{O_2}$  approximately constant,  $D_W^{met/sil}$  shows a small range of 60-100, in contrast to changes of many orders of magnitude found when composition and  $f_{O_2}$  vary [8-12]. C capsules form carbides above 1600°C. W concentration in the silicate plummets because

$D_W^{carbide/sil} \gg D_W^{met/sil}$ . If this process affected the high-T study of [10], the apparently higher  $D_W^{met/sil}$  of [10] compared to studies at moderate T are explained. Multiple linear regressions [e.g. 13] edited to remove the data of [10] should give decreasing  $D_W^{met/sil}$  (instead of increasing) as T increases! If  $D_W^{met/sil}$  did increase with T, only unrealistically cool magma oceans could dissolve the present mantle W abundances. This difficulty is removed with exclusion of the carbide-biased data.



● Borisov and Palme, 1997 and Ertel et al., 1999 (1 bar, 1300-1500°C) — Fortenfant et al., 2003 extrapol in T (1 bar)  
 ▲ Holzheid et al., 2000 (1-16 GPa) — measured (1 bar)  
 ● This Study (2 GPa) 2500°C shown in (a)

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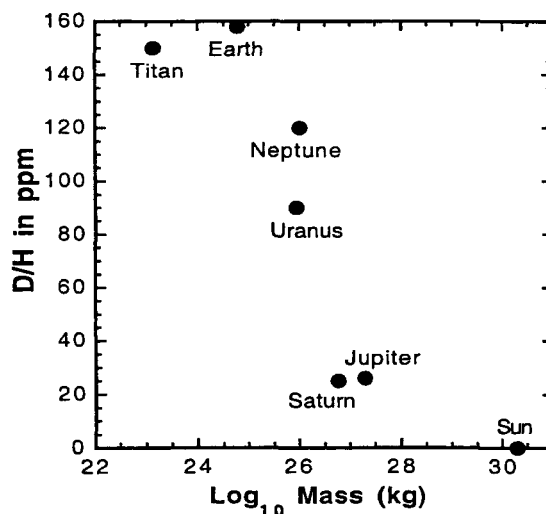
# TERRESTRIAL OXYGEN AND HYDROGEN ISOTOPE VARIATIONS: PRIMORDIAL VALUES, SYSTEMATICS, SUBSOLIDUS EFFECTS, PLANETARY COMPARISONS, AND THE ROLE OF WATER

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**Introduction:** O and H isotopic variations provide key information on planetary formation and the evolution and interactions of their lithospheres, atmospheres and hydrospheres. Earth is best understood. The  $\delta^{18}\text{O}$  values of Earth's major lithospheric reservoirs such as MORB closely approximate those of lunar igneous rocks ( $+5.7 \pm 0.3$  ‰). This similarity suggests that Earth and Moon have a common primordial affinity and that  $+5.7$  ‰ is the bulk  $^{18}\text{O}$  composition in the Earth-Moon system, but only Earth's outermost layers have been sampled. Also, large total  $^{18}\text{O}$  ranges are observed for terrestrial magmas ( $-2$  to  $+16$  ‰, ref [1]), igneous rocks ( $-10.5$  to  $+16$  ‰), and sedimentary rocks (at least  $-4$  to  $+39$  ‰). Only small effects ( $< 2$ ‰) can be attributed to pure fractional crystallization as isotopic fractionations are small at high temperatures; this partly explains why felsic rocks are systematically higher in  $^{18}\text{O}$  by 1-4 per mil than mafic and ultramafic rocks, but cannot explain the total ranges in terrestrial rocks. Earth's great ranges therefore require interaction or exchange of rocks and magmas with oxygen reservoirs at or near Earth's surface, where large enrichments or depletions in  $^{18}\text{O}$  are possible because fractionation factors are large at low temperatures. Key identified processes include aqueous deposition, subsolidus exchange with infiltrating hydrothermal fluids, and exchange with or assimilation of wallrocks having disparate compositions. Open and closed subsolidus processes are easily distinguished on  $\delta$ - $\delta$  plots, as they respectively create positive and negative-sloped trends in most cases [2]. Meteorites commonly feature pronounced disequilibrium effects but rarely show trends suggesting that coherent suites underwent subsolidus exchange.

The  $\delta\text{D}$  values of most sedimentary, metamorphic and igneous rocks on Earth are  $-40$  to  $-95$  ‰, a similarity indicating that subduction of hydrous sediments, followed by dehydration and recycling, has considerably homogenized the D/H ratio of Earth's outer layers [1]. These rock reservoirs plus the huge hydrosphere together comprise Earth's hydrogen inventory that accordingly has a bulk  $\delta\text{D}$  value of about  $-20$  ‰ rel SMOW, or 160 ppm. Earth's D/H ratio is much higher than that of the outer atmospheres of gas giants that are as low as  $\sim 20$  ppm. This difference is commonly attributed to atmospheric loss of terrestrial protium over geologic time, a mechanism that provides a convenient partial explanation for Earth's high oxidation state. In fact, the D/H ratios of planets correlate with their mass, suggesting that deep levels in the gas giants have much higher D/H than their outer atmospheres (Figure; data from [3] but Uranus and Neptune are uncertain). If so, Earth's D/H ratio may be the best representative of the primitive solar system value.

Oxygen isotope relations are codified in a "three-isotope" plot of  $\delta^{17}\text{O}$  vs.  $\delta^{18}\text{O}$  values. On this diagram, individual planets and meteorite types define striking parallel line segments whose 1) slope of  $\sim 0.53$  is the theoretical mass-dependent fractionation trend; 2) y-intercept is the  $\Delta^{17}\text{O}$  parameter; 3) center of mass is the bulk isotopic composition of the planet or family, and 4) length defines the extent to which the body or family has been fractionated into various reservoirs of disparate composition. Of these characteristics, the mass-dependent slope is best understood and, for three isotopes of any element having masses of  $m_1$ ,  $m_2$  and  $m_3$ , is precisely equal to:  $m_3(m_2 - m_1)/(m_2(m_3 - m_1))$  [ref 4]. The  $\Delta^{17}\text{O}$  value indicates the relative position of the lines and tends to increase with the K/U ratio and other ratios of volatile and refractory elements, likely representing a combination of chemical controls such as heliocentric distance and time of initial condensation. Segment length primarily reflects the effect of secondary fractionation processes, and would be enhanced by low T and by interactions of solids with liquids or gas; samples with high  $\delta^{18}\text{O}$  values commonly have high water contents. Earth is most highly fractionated, due to its protracted igneous evolution, low surface temperature, and the extensive interactions of its dynamic lithosphere with its large hydrosphere.



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**REDOX STATE OF THE MOON'S INTERIOR.** J. W. Delano, Dept. of Earth and Atmospheric Sciences, and Dept. of Chemistry, The University at Albany (SUNY), Albany, NY 12222 jdelano@atmos.albany.edu

The redox state of the lunar interior is constrained by analyses of endogenous melts that have ascended to the lunar surface from depths of at least 400 kilometers. Lunar volcanic rocks (i.e., crystalline mare basalts and picritic volcanic glasses) are characterized by low oxidation states (i.e., ~1-2 log-units below the iron-wustite (IW) buffer [e.g., 1-15]), as indicated by the presence of Fe-rich metal [e.g., 4], occurrence of  $Ti^{3+}$  in armalcolite [e.g., 7,11,16], the high abundance of Cr, and the inferred dominance of Cr in the  $Cr^{2+}$  valence state [e.g., 12]. While it is considered likely that the observed redox states of lunar volcanic rocks and lunar volcanic glasses reflect the redox state of the Moon's interior, suggestions have been made that near-surface processes during eruption may have imposed late-stage overprints on the oxidation states that cause the observed redox states to differ from that of the Moon's interior. Open-system processes that have been suggested as having altered the original, pre-eruptive redox states of the lunar magmas during eruption include reduction by 'oxygen pumping' [e.g., 2,8,9], reduction by sulfur loss [e.g., 5,13,17,18], reduction by addition solar wind  $H_2$  from regolith [e.g., 19], reduction by carbon at low pressure [e.g., 15], reduction of loss of carbonyl sulfide, COS [e.g., 15], and oxidation by alkali loss [e.g., 9].

Reduction by sulfur loss:  $2FeS = 2Fe^0 + S_2$

Reduction by solar wind  $H_2$ :  $FeO + H_2 = Fe^0 + H_2O$

Reduction of COS:  $FeS + FeO + C = 2Fe^0 + COS$

Oxidation by alkali loss:  $2Na_2O = 4Na + O_2$

Current views are that the observed redox states of lunar volcanic samples are either due to (a) equilibrium between a Fe-rich metal phase (e.g., metallic core) and Fe-rich silicates (e.g., mantle), or (b) buffering by C-CO-CO<sub>2</sub>.

The observation that high P,T melting experiments on lunar magmatic compositions remained chemically unchanged when contained in high-purity Fe capsules [e.g., 20] is consistent with the former view. In addition, if lunar picritic glasses originated from source regions at pressures ~20 kbars (~2 GPa) in the Moon [e.g., 21-23], the pressure-dependence of the C-CO-CO<sub>2</sub> buffer would cause the redox state at those pressures in the Moon to be ~1.5 log-units  $fO_2$  above the iron-wustite buffer. The consequence of that oxidation state, if picritic magmas were saturated with a Cr-rich spinel phase in the source-region

mineral residues, would be that the Cr abundances in the primary magmas would be ~2500 ppm, instead of the observed ~4000 ppm. The high Cr abundances in lunar picritic glasses and mare basalts (~4000 ppm) are consistent with their having originated at high pressures (~2 GPa) at a redox state of ~1-2 log-units  $fO_2$  below the iron-wustite buffer, if those magmas were saturated with a Cr-rich spinel in their source-regions [e.g., 24-26].

These two chemical processes (i.e., metal/silicate equilibrium; C-CO-CO<sub>2</sub> buffer) that have been proposed for controlling the oxidation state of the Moon's interior deserve closer scrutiny. Their implications for the redox state of the deep lunar interior are significantly different.

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**HOW DID THE TERRESTRIAL PLANETS ACQUIRE THEIR WATER?** M. J. Drake, M. Stimpfl, and, D. S. Lauretta, Lunar and Planetary Laboratory, University of Arizona, Tucson, Arizona 85721-0092, U.S.A. drake@lpl.arizona.edu

**Introduction:** There is no consensus on the origin of water in the terrestrial planets. Earth demonstrably has water. Odyssey has shown vast water ice sheets buried under a thin layer of dust polewards of about 60° of latitude in both hemispheres of Mars [1]. The D/H ratio of Venus is about 100 times that of Earth's oceans [2], and is plausibly explained by loss of H<sub>2</sub>O through UV photodissociation at the top of the Venus atmosphere. Mercury and the Moon appear to be bone dry, possibly due to volatile loss in giant impacts.

**Sources of water:** It has generally been thought that the accretion disk was too hot at 1 AU for hydrous minerals to be stable, although the thermal history of the inner disk is based on models, not observations. Comets had been a popular choice for the source of water, as they demonstrably contain water ice. However, the measured D/H ratios in Hale-Bopp, Hyakutake, and Halley are identical within error and, if these measurements are representative of bulk comets, they constrain the contribution of cometary water to less than 15%. The ratio of Ar/H<sub>2</sub>O in comet Hale-Bopp and Ar/O in comet LINEAR imply still lower limits on cometary water if the spectral measurements are reliable. Asteroids are dynamically plausible sources of water, but Os isotopes in Earth's mantle rule out known meteorite types as the source of Earth's water. See Drake and Righter [3] for a more thorough discussion. Inward migration of phyllosilicates has also been proposed [4].

**Indigenous source revisited:** Let us accept for now that the inner accretion disk was too hot for hydrous minerals to be stable and consider an alternative source of H<sub>2</sub>O. The dust in the disk was bathed for some time in a sea of H and O. The amount of water vapor present in the accretion disk within 3 A.U. equaled about three times the Earth's mass [5].

**Adsorption:** It is possible that water from the gas phase could be adsorbed onto grains in the inner solar system and subsequently accreted into the terrestrial planets. Stimpfl *et al.* [6] modeled the adsorption of water from 1500K to 1000K using a Monte Carlo simulation with a grid of 10000 adsorption sites, and an iterative process allowing the surface to reach steady state saturation at each temperature. Water molecules not only interact with the substrate by means of weak bonds (~5kJ/mole) but also establish hydrogen bonds with other water molecules present in a monolayer [7]. The energy of the incoming molecules was computed using the Maxwell-Boltzmann probability distribution. We allowed only for the adsorption of one monolayer, neglected porosity and surface roughness, considered water an

infinite reservoir, and assumed that all the particles interacting with the surface were water molecules.

We pulverized the Earth into homogenous spheres of 0.1 m radius. The adsorbed water potentially stored in the dust corresponds to ~3 times the Earth's oceanic + atmospheric + crustal water (OAC) [8] and ~1.5 times the Earth's OAC + mantle water [8]. If the grain size increases, however, the amount of water adsorbed on the surface decreases; in this model the biggest grain size that allows for 1 Earth's OAC water to be adsorbed is ~0.3 m. On the other hand, porosity and surface roughness would increase the number of adsorption sites as well as shelter adsorbed molecules from bombardment.

**Non-mineral bonding:** Ab initio calculations at 0°K in which the Gibbs free energy of Si - O clusters is minimized and then a H<sub>2</sub>O molecule is introduced indicate that strong chemical bonds can be formed between the water molecule and the Si - O cluster [9], making retention of H<sub>2</sub>O during the later violent stages of accretion more likely. These calculations need to be conducted at realistic nebular temperatures.

**Conclusions:** These considerations suggest that H<sub>2</sub>O may have been obtained by the terrestrial planets directly from the gas phase in the accretion disk. The initial water budgets would be functions of P and T and, hence, heliocentric distance. Accretion of water in the presence of metal will lead to extraction of H into planetary cores and progressive oxidation of planetary mantles [10, 11]. The "feeding zones" of the terrestrial planets would be relatively narrow over most of planetary accretion, consistent with differences in O-isotopes, Cr-isotopes, and major element compositions of Earth and Mars [3]. The "late veneer" could plausibly be of asteroidal origin, consistent with dynamical calculations [8].

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**MOLECULAR OXYGEN MIXING RATIO AND ITS SEASONAL VARIABILITY IN THE MARTIAN ATMOSPHERE.** C. England<sup>1</sup> and J. D. Hrubes<sup>2</sup>, <sup>1</sup>Jet Propulsion Laboratory, 4800 Oak Grove Dr., Pasadena, CA 91109, cengland@jpl.nasa.gov, <sup>2</sup>Raytheon Polar Services, Amundsen-Scott South Pole Station, cusplab@usap.gov.

**Abstract:** The mixing ratio of molecular oxygen and other species that do not condense at martian ambient conditions will vary as the mass of atmosphere oscillates over a martian year due to alternate condensation and vaporization of carbon dioxide at the poles [1]. This variation can be estimated utilizing measurements of mixing ratio made *in-situ* together with multi-year measurements of atmospheric pressure, both available from the Viking landers starting in 1976. The concentration of non-condensables, on average, will be approximately an inverse function of the atmospheric pressure.

Viking Lander 1 (VL1) measured atmospheric pressure at the surface of Mars at 22.3° north latitude and 48.0° longitude for approximately 3¼ martian years [2]. Three *in-situ* measurements for molecular oxygen are reported, all from the Viking landers. The first was from the neutral mass spectrometer (NMS) during VL1's entry, measured at 135 km, providing a mixing ratio of 0.003, or 0.3% [3]. The other two determinations were from VL1's gas chromatograph/mass spectrometer. Both were reported as unreliable but as bracketing the mixing ratio of molecular oxygen between 0.1%–0.4% [4]. No values were reported from instruments on Viking Lander 2.

A later summary [5] provided an estimate of atmospheric composition at the martian surface, suggesting a mixing ratio for oxygen of 0.13%, a value that is very often cited as the accepted value [1,6]. This value, however, appears to have its origin from two Earth-based measurements made prior to the Viking mission, and might be considered less dependable than the VL1 NMS *in-situ* measurement [5,7,8].

Figure 1 plots the mixing ratio of molecular oxygen over a full martian year by inverse scaling with the atmospheric pressure, and by utilizing the VL1 entry value (0.3%) and date of entry (areocentric longitude of 97.04°). This relationship is implied by the expected near-exclusion of molecular oxygen and other low-boiling species in the condensed phase at the poles.

The highest molecular oxygen concentration is 0.34%, occurring at the period of lowest atmospheric pressure and smallest atmospheric mass at an areocentric longitude of about 145°. This value is markedly higher than the commonly cited value of 0.13%, and may suggest additional analysis is warranted to understand the compositional behavior of the martian at-

mosphere. The smallest predicted concentration is 0.25% at about 261°.

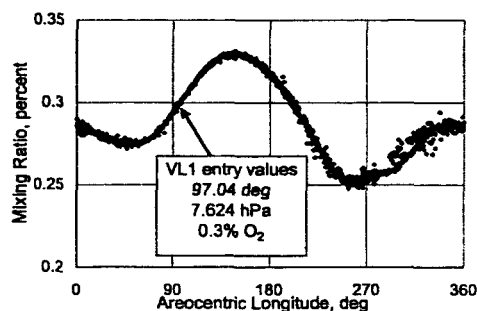


Fig. 1. Seasonal Variation of Mixing Ratio of O<sub>2</sub>

Other non-condensing species will experience similar variation that can be estimated by simple proportions. Carbon monoxide, an important compound in the understanding of martian atmospheric chemistry, has not yet been measured *in-situ*, and its mixing ratio remains highly uncertain.

Figure 1 illustrates the global average mixing ratio of oxygen since the amount of non-condensing species will vary locally as they are selectively concentrated and then expelled from the poles during the condensation-sublimation cycle. While it can be argued that the measurement for molecular oxygen at 135 km may not be fully representative of surface concentration, Figure 1 assumes no significant differentiation of neutral species is likely at the fractional percent level. If oxygen is present at the levels suggested, direct extraction from the martian atmosphere for use as a propellant for sample or crew return as well as for breathing may be practical [9].

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**EXCHANGE BETWEEN THE ATMOSPHERE AND THE REGOLITH OF MARS: DISCUSSION OF OXYGEN AND SULFUR ISOTOPE EVIDENCE.** J. Farquhar ESSIC and Department of Geology, University of Maryland, College Park, Maryland, 20742 (jfarquha@essic.umd.edu).

**Introduction:** Mass-independent fractionations for oxygen isotopes and sulfur isotopes between secondary phases and primary igneous phases in SNC meteorites have been interpreted to reflect a difference between surface and deep oxygen and sulfur reservoirs on Mars [1-6]. Several hypotheses have been proposed to explain this observation such as fractionation by escape processes (in the case of oxygen), addition of a late veneer of anomalous oxygen and sulfur, and mass-independent atmospheric chemistry [1, 4, 5, 7, 8]. The observation of a variable magnitude mass-independent oxygen isotope signature for carbonate and water among different meteorites, and for carbonate and sulfate from the same meteorite (Nakhla) is most consistent with the latter interpretation.

Narrowing the source of the sulfur isotope data is less straightforward but bears on the question atmosphere-surface oxygen exchange because it may reflect a similar process. The magnitude of the mass-independent fractionations for sulfate sulfur from Nakhla and for isolated grains in ALH84001 [1, 3] are larger than those seen for all analyses of whole rock sulfide and sulfate from other meteorite groups (e.g., [9-11]). This argues against an origin associated with addition of a late veneer of exotic sulfur. Experimental and theoretical evidence allows a gas-phase (atmospheric) origin for these mass-independent sulfur and oxygen isotope signals [12], and the observation of mass-independent sulfur isotope signatures in atmospheric and atmospheric-derived species on Earth [13] provides a consistency argument in favor of similar processes operating on Mars. Mass-independent oxygen and/or sulfur isotope signatures have been observed in terrestrial sulfate aerosols, ice core sulfate from stratosphere-piercing volcanic eruptions, and terrestrial rock samples older than 2.0-2.5 billion years old [3, 12, 14, 15]. For sulfur, these signatures are larger than the largest that have been identified in the meteoritic record and direct transfer of atmospheric sulfur species such as sulfate to the surface has been suggested as the source for the SNC signature. (Minor components of some carbonaceous chondrites have been shown to possess mass-independent signatures up to a few permil.)

The Earth-centered perspective also tells us that the exchange pathways and local reservoir sizes for oxygen and sulfur can play a significant role in the transfer and preservation of these signals in the rock record leading to the interpretation that the sulfur and oxygen isotope signature in sulfate sulfur may reflect direct

transfer of the sulfate from the atmosphere to the surface, but that the oxygen isotope signatures for carbonate and water may reflect the transfer of oxygen from another species that itself acquired a mass-independent oxygen isotopic composition from the atmosphere.

Consideration of the amounts of oxygen in the carbonate and water, leads to the suggestion that the isotopic composition of both species was buffered by an oxidized species in the regolith that itself had a mass-independent oxygen isotopic composition. This oxidized species may have been directly deposited to the regolith, or formed by oxidation of another species by reaction with a mass-independent species like ozone. The signature would then be transferred from the water to the carbonate during carbonate formation. In the case of SNC carbonate, this interpretation would imply that the amounts of aqueous phase were limited, or at least comparable to the amounts of the phases in the regolith with which they exchanged oxygen. The significance of this observation for the Martian surface oxygen reservoirs is that it suggests the absolute amounts of oxygen stored in liquid phase water may have been small, and that transfer of oxygen between phases in the regolith and the martian atmosphere is a common phenomenon. The observation of this signature in carbonate from ALH84001 suggests that the conditions required for the production and preservation of these signals in the SNC record extend were established early in Mars's history.

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**OXYGEN AND HYDROGEN ISOTOPE SYSTEMATICS OF ATMOSPHERIC WATER VAPOR AND METEORIC WATERS: EVIDENCE FROM NORTH TEXAS .** K. M. Ferguson<sup>1</sup> and R. T. Gregory<sup>1</sup>, <sup>1</sup>Stable Isotope Laboratory, Department of Geological Sciences, SMU PO Box 750395, Dallas TX 75275; kferg@smu.edu

**Introduction:** Understanding the relationship between surface temperature and the oxygen and hydrogen isotopic composition of meteoric water is critical for unraveling the climate history of the Earth. The correlation between mean annual temperature and the isotopic composition of precipitation forms the basis of interpretation of temperature fluxations in ice core data and hence some similar relationship may obtain for a planet like Mars. The signal inferred from ice measurements correlates with oxygen isotope ratios determined from marine sediments that documents 450,000 years of glacial-interglacial cycles [1].

**Why Dallas?:** Dallas, Texas, sits in the pathway of Polar, Pacific, and Gulf of Mexico air masses. Stable isotopes being a conservative tracer provide an opportunity to track the time integrated history of air masses interacting over Dallas. Isotopic concentration data provide hard constraints on storm and air mass evolution currently modeled by weather forecasting programs and global circulation models.

**Methodology:** For the years 2001-2003, we sampled individual precipitation events over periods lasting between minutes to hours to examine intrastorm isotopic ratio variability in the context of satellite and radar images taken over the same time intervals. In order to gain a more continuous record, we began monitoring the isotopic composition of the atmospheric water vapor at approximately 30 m above the ground on a daily basis.

**Results:** Over the 2+ year period, our data capture a good portion of the temperature-water isotope variability of the International Atomic Energy Agency data set, e.g., [2]. Despite  $^{18}\text{O}$  values ranging from +8 to -18 permil, there is only a weak correlation with temperature for most storms, or for longer term time averages. Meteoric waters define meteoric water lines of:

$$D = 7.01 \text{ } ^{18}\text{O} + 8.29 \text{ } R^2 = 0.90 \text{ } 2001$$

$$D = 7.13 \text{ } ^{18}\text{O} + 7.61 \text{ } R^2 = 0.93 \text{ } 2002$$

Distribution diagrams for isotope data for these two years show slightly different means (2001 mean  $^{18}\text{O}$  = -4.0, n = 433; 2002 mean  $^{18}\text{O}$  = -5.0, n = 517), suggesting different proportions of Gulf moisture (the dominant source) and more  $^{18}\text{O}$ -depleted Polar or Pacific sourced moisture. In D- $^{18}\text{O}$  plots, cloud bands exhibit distinctive isotopic evolution suggesting that water vapor maintains isotopic heterogeneities over significant distances and further suggesting stirring without homeogenization by mixing. Comparison of the values of the water vapor against 1/concentration

suggests two end-member behaviors: 1) isotopic depletion by advection between air masses of different provenance and 2) isotopic depletion by distillation (rain-out effect). Comparison of isotopic data from storm events with satellite imagery provides evidence of the relative importance of the two end-member processes. An example is shown in Figure 1 for February 15-16, 2001. The 4.5 permil oxygen isotope depletion in the early morning of Feb. 16 occurred over approximately 2 hours, with no correlation between surface air temperature and  $^{18}\text{O}$ . Satellite imagery of the storm suggests at least part of the depletion event may result from advection of higher altitude, isotopically depleted air towards the surface.

The dominant source of moisture for Dallas meteoric water is from the Gulf of Mexico, not necessarily clear from examination of satellite images. During intense rainout events, on rare occasions, evidence of mixing with supercooled or  $^{18}\text{O}$ -depleted upper air masses is inferred by changes in the slope and intercept of the meteoric water line during huge collapses of the unstable air mass.

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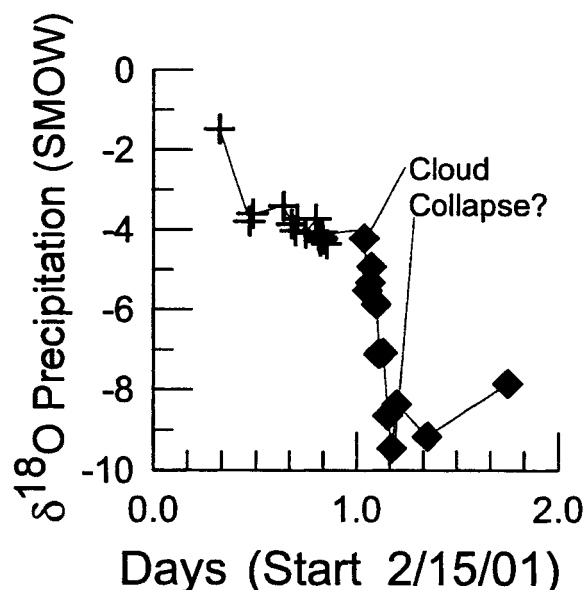


Figure 1.  $^{18}\text{O}$ -time graph for storm of February 15-16, 2001. Crosses represent meteoric water samples from Feb. 15, filled diamonds samples from Feb. 16.



**IMPLICATIONS OF ISOTOPIC AND REDOX HETEROGENEITIES IN SILICATE RESERVOIRS ON MARS.** C. N. Foley<sup>1</sup>, M. Wadhwa<sup>1</sup>, L. Borg<sup>2</sup>, and P. E. Janney<sup>1</sup>, <sup>1</sup> Isotope Geochemistry Laboratory, Department of Geology, The Field Museum, 1400 S. Lake Shore Dr., Chicago, IL 60605, [nfoley@finnh.org](mailto:nfoley@finnh.org). <sup>2</sup>Institute of Meteoritics, University of New Mexico, Albuquerque, NM 87131.

**Introduction:** New constraints on Nd and W isotopic systematics [1] show that there is no simple linear relationship between  $\epsilon^{142}\text{Nd}$  and  $\epsilon^{182}\text{W}$  values in the Martian meteorites as was suggested by [2] based on earlier data [2, 3]. Instead, three distinct end-members are apparent: LREE-enriched shergottites, such as Shergotty and Zagami, which have chondritic  $\epsilon^{142}\text{Nd}$  and superchondritic  $\epsilon^{182}\text{W}$  ( $\sim 0\epsilon$  and  $\sim 0.5\epsilon$ , respectively, relative to terrestrial); LREE-depleted shergottites, such as DaG 476, with superchondritic  $\epsilon^{142}\text{Nd}$  and  $\epsilon^{182}\text{W}$  ( $\sim 0.9\epsilon$  and  $\sim 0.5\epsilon$ , respectively, relative to terrestrial); and the nakhlites-chassignite (NC) with superchondritic  $\epsilon^{142}\text{Nd}$  and  $\epsilon^{182}\text{W}$  ( $\sim 0.7\epsilon$  and  $\sim 3\epsilon$ , respectively, relative to terrestrial). These systematics reveal that early differentiation events on Mars resulted in the formation of at least three distinct silicate reservoirs which have subsequently remained unaffected by global convective mixing. In particular, as discussed in [1], core formation occurred early (within  $\sim 12$  Ma from the beginning of the solar system) followed by a silicate differentiation event ( $\sim 20$ - $25$  Ma after solar system formation) which established a mantle reservoir with the unique NC source characteristics; continued silicate differentiation (extending  $>45$  Ma after solar system formation, when  $^{182}\text{Hf}$  was extinct but  $^{146}\text{Sm}$  was extant) resulted in the formation of two end-member silicate reservoirs involved in shergottite petrogenesis, i.e., a depleted mantle reservoir and an enriched (mantle or crustal) reservoir. Here we will discuss the constraints on the redox conditions in these three isotopically distinctive silicate reservoirs and how they may relate to their isotopic characteristics.

**Shergottite isotopic and redox systematics:** The basaltic shergottites record a range of magmatic redox conditions [4, 5, 6]. It has been suggested that the apparent correlation of magmatic redox conditions with other geochemical and isotopic parameters (such as initial  $^{87}\text{Sr}/^{86}\text{Sr}$  and  $^{143}\text{Nd}/^{144}\text{Nd}$  ratios and the degree of LREE-enrichment in the shergottite whole rocks) indicates that this range may result from the assimilation of varying amounts of an oxidized crust-like component by melts derived from a depleted, reduced mantle reservoir [4, 6]. In this scenario, the oxidation of the crust-like component may have occurred at any time prior to its assimilation into the mantle derived melts.

Alternatively, variations in the oxygen fugacities of shergottite magmas may reflect the mixing of melts derived from depleted and enriched mantle sources that were the crystallization products of an ancient magma ocean [7]. In this scenario, the redox conditions in the depleted (reduced) and enriched (KREEP-like, hydrous and oxidized) sources were established early, at the

time of magma ocean crystallization. These two alternatives have implications for the timing at which redox heterogeneities in silicate reservoirs on Mars were established. As discussed by [7], the decoupling of major element and trace element-isotopic systematics in the shergottites supports the latter scenario, and could indicate that isotopic and redox heterogeneities in the two shergottite end-member sources are causally related and were established early.

**Nakhlite isotopic and redox systematics:** The nakhlites show isotopic and redox systematics that are quite distinct from the shergottites. As mentioned earlier,  $^{147,146}\text{Sm}$ - $^{143,142}\text{Nd}$  and  $^{182}\text{Hf}$ - $^{182}\text{W}$  isotope systematics in the nakhlites indicate that their source was established prior to the two shergottite end-member sources discussed above [1]. Moreover, while the initial  $\epsilon^{143}\text{Nd}$  values for the nakhlites suggest a long-term depletion in the nakhlite source [8], the estimated parent melt compositions for these pyroxenites are LREE-enriched [9,10]. Finally, estimations of magmatic redox conditions for the nakhlites indicate that they originated from an oxidized source (close to  $\sim\text{QFM}$ ) [10,11].

Therefore, while the depleted shergottite end-member mantle source was highly reduced, the depleted (and isotopically distinct) nakhlite source was relatively oxidized. It has been suggested that the decoupling of the isotope and trace element systematics in the nakhlites may be accounted for by late metasomatism of the nakhlite source by an LREE-enriched fluid [7,10]. Late mantle metasomatism by an LREE-enriched, oxidizing (possibly hydrous) fluid could also account for the oxidation of the nakhlite source.

**Implications:** The main implication from the above discussion is that redox conditions of mantle sources on Mars may largely have been established early (most likely during crystallization of the ancient magma ocean). However, late mantle metasomatism may have subsequently modified the redox conditions in some of the early established mantle reservoirs.

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**OXYGEN ISOTOPIC VARIATION OF THE TERRESTRIAL PLANETS.** I. A. Franchi and R. C. Greenwood, Planetary and Space Sciences Research Institute, Open University, Walton Hall, Milton Keynes, MK7 6AA, UK (i.a.franchi@open.ac.uk)

**Introduction:** Since the seminal work of Clayton and co-workers [1] it has been clear that there was oxygen isotopic heterogeneity in the most primitive materials in the solar nebula, with variations of up to 50‰ in  $\Delta^{18}\text{O}$  and over 25‰ in  $\Delta^{17}\text{O}^1$  in materials formed or at least heavily processed within the nebula. In the terrestrial planets (Earth, Moon, Mars and the HED parent body (possibly Vesta)) the range in  $\Delta^{18}\text{O}$  values can remain very large, especially on geologically active bodies, particularly the Earth where low temperature reactions with water can play an important role in developing large isotopic variations. However, the variation that is now seen in  $\Delta^{17}\text{O}$  is <1‰ [e.g. 3], with the variation from each body generally much less. This limited range in the  $\Delta^{17}\text{O}$  values is generally believed to be the result of large volume homogenization during widespread heating/melting events during the history of these planets and large asteroids. However, variation still exists within and between the suites of rocks from each of the terrestrial planets, and this can provide valuable information on their origin, inter-relationship and evolution. In order to extract this information it is necessary to measure the oxygen isotopic composition of clean, well characterised materials to very high precision.

We have undertaken a number of studies covering most the main sample suites from evolved planets or asteroids using a technique of laser ( $\text{CO}_2$  laser @ 10.6µm) assisted fluorination ( $\text{BrF}_3$ ) coupled to a high dispersion, high precision mass spectrometer (VG PRISM III). This offers analytical precision for  $\Delta^{18}\text{O}$  and  $\Delta^{17}\text{O}$  of 0.08 and 0.04‰ respectively, but as much of this uncertainty is related to gas handling fractionation the  $\Delta^{17}\text{O}$  uncertainty is <0.025‰ [4] and allows us to determine mass fractionation lines with uncertainties down to  $\pm 0.013\%$  [e.g. 5] –

approximately 50 times smaller than the variation displayed by the terrestrial planets/asteroids.

**Oxygen Isotope Variation:** Within the limited range of  $\Delta^{17}\text{O}$  values displayed by samples of the terrestrial planets three broad grouping could readily be discerned – Mars, the Earth/Moon and the basaltic meteorites (HEDs, angrites, plus various other meteorite types) [3] allowing discrimination of the groups, useful in the classification of new meteorites, and offering insight into the degree of homogenization and into the identification of the relative contributions of possible primitive precursors. High precision analyses have revealed considerable more detail to this initial picture. The SNC meteorites define a martian fractionation line with a  $\Delta^{17}\text{O}$  value of  $+0.032 \pm 0.01$  [5]. The basaltic meteorites (HEDs and angrites) previously defined what appeared to be a single, albeit relatively poorly defined mass fractionation line. However, as shown in Figure 1 the HEDs define what appears to be a well defined fractionation line ( $\Delta^{17}\text{O} = -0.24 \pm 0.007$ ) with the angrites ( $\Delta^{17}\text{O} = -0.072 \pm 0.007$ ) now clearly resolved. In contrast, high precision measurements of lunar rocks by Wiechert et al [6] shows that there is no isotopic difference between the Earth and the Moon.

**Discussion:** While the oldest, and possibly least precise of the high precision data the SNC meteorites clearly define a single martian fractionation line. Virtually all martian meteorites have relatively young crystallization ages but the data set includes ALH 84001, a sample of ancient crust with a crystallization age of approx 4.5Ga. As such it is clear that homogenisation of any initial isotopic heterogeneity occurred within the first few tens of millions of years after formation [5]. Even more rapid melting and homogenization may be required for 4 Vesta (HEDs) as all but one (Pasamonte) of the eucrites and diogenites fall on a single mass fractionation line, despite the fact that there are several geologically distinct groups with different histories within the eucrites. The anomalous nature of Pasamonte was also detected by [7] who also reported two other meteorites with similar  $\Delta^{17}\text{O}$  values – suggesting that in fact some isotopic heterogeneity was retained within Vesta as cooling progressed. It may be that these anomalous eucrites are not from the same parent body, or were contaminated by impactor material or that homogenization was not complete.

<sup>1</sup> Virtually all physical processes acting upon any homogeneous reservoir of oxygen, will have an impact on the  $^{16}\text{O}/^{17}\text{O}$  ratio approximately 0.52 times that of the effect on the  $^{16}\text{O}/^{18}\text{O}$  ratio – such that on a three isotope plot ( $\Delta^{17}\text{O}$  vs  $\Delta^{18}\text{O}$ ) any such suite of samples resulting from this reservoir would plot upon a line of slope 0.52 [2]. The  $\Delta^{17}\text{O}$  value is defined as the offset from such a line defined by crustal and mantle rocks from Earth ( $\Delta^{17}\text{O} = \Delta^{17}\text{O} - (0.52 * \Delta^{18}\text{O})$ )

Further detail on the geochemical similarities and differences between the oxygen isotope populations within suites of similar basaltic rocks will go a long way to helping to resolve this problem, but will also shed considerable light on the structure of this body as it formed.

The angrite meteorites are another suite of ancient basaltic meteorites. Geochemically distinct from the HEDs, they are now clearly resolved on the basis of oxygen isotopes as well. With very ancient crystallization ages homogenization of the angrite parent body must have been very rapid. It should be noted that a fairly typical eucrite (Ibitira) has a  $\Delta^{17}\text{O}$  value indistinguishable from the angrites – which raises the question as to whether a geological relationship exists between the angrites and (at least) some of the eucrites.

Other examples of the use of high precision oxygen isotope analysis includes the complete similarity in the  $\Delta^{17}\text{O}$  value of the Moon and the Earth which has been taken to show that the Earth and Theia (putative Moon-forming Earth impactor) were formed from the same material, presumably at a similar heliocentric distance [6].

High precision oxygen isotopic measurements are required on a number of other groups with close associations with the basaltic meteorites (e.g. the mesosiderites) in order to determine if they have distinguishable isotopic reservoirs, and in combination with detailed geochemical data determine if these reservoirs originate on a single or discrete parent bodies.

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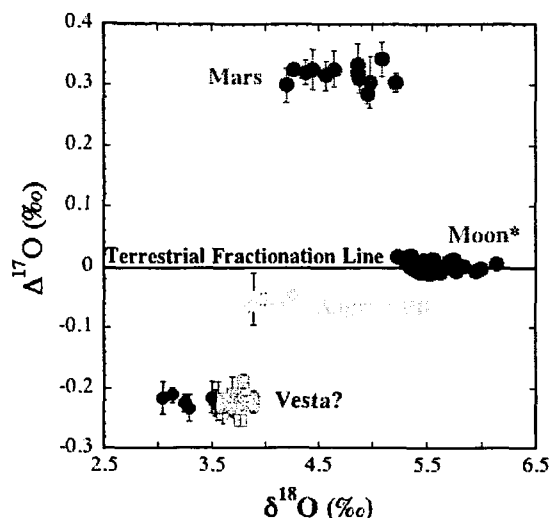


Figure 1 – Oxygen isotopic variation of the terrestrial planets. On this modified version of a three isotope plot mass fractionation lines (constant  $\Delta^{17}\text{O}$ ) plot as horizontal lines. Terrestrial data not shown as this spans a very large range in  $\Delta^{17}\text{O}$  but has a similar scatter to lunar and martian data sets [e.g. 5,7]. Lunar data from [6].

**REDOX EXCHANGES IN HYDROUS MAGMA.** F. Gaillard<sup>1</sup>, B.C. Schmidt<sup>1</sup>, C. A. MacCammon<sup>1</sup>, M. Pichavant<sup>2</sup>, B. Scaillet<sup>2</sup> and S.J. Mackwell<sup>3</sup>. <sup>1</sup>Bayerisches Geoinstitut, Universitt Bayreuth, D-95440, Bayreuth, Germany; <sup>2</sup>ISTO, 1A rue de la Ferrollerie, 45071 Orleans cedex 2, Orléans, France; <sup>3</sup>Lunar and Planetary Institute, 3600 Bay Area Boulevard, Houston, TX 77058.

**Abstract:** Contrasts in redox conditions prevailing in magma within the Earth have been and are still responsible for extensive large-scale chemical differentiation during the past 4.6 billion years. The formation of the core is likely attributable to a primary magma ocean in equilibrium with Fe-metal in the early age of the Earth [1]; the oceanic crust is constructed by accretion of mid-ocean-ridge-basalt containing dominantly ferrous iron [2]; and the continental crust probably derives from subduction-related arc-magmas that contain ~20-60% of iron in the ferric form [3]. These redox controls on the magma-derived stratification of the Earth underline the need for a fundamental understanding of mechanisms and rate of redox exchanges in natural silicate melts.

The redox state of a melt is commonly associated with its iron redox ratio  $\text{Fe}^{3+}/\text{Fe}^{2+}$  and correlated to the intensive parameter oxygen fugacity,  $f\text{O}_2$ . Since the 1960s, numerous experimental studies have contributed to the calibration of the thermodynamic relationship between  $f\text{O}_2$ ,  $\text{Fe}^{3+}/\text{Fe}^{2+}$ ,  $T$ , and chemical composition of the silicate liquid [4-5]. In contrast, the nature of the rate and mechanisms of acquisition of redox state in anhydrous melts has only been recently elucidated and it has been shown that migration of both monovalent and divalent cations rate-limits the kinetics of iron oxidation-reduction in silicate melts [6]. However, natural silicate melts contain water in the range of hundred of ppm to several wt% [7], which contribute, in comparison to anhydrous systems, an additional redox couple,  $\text{H}_2 / \text{H}_2\text{O}$ . Due to the great mobility of both  $\text{H}_2$  and  $\text{H}_2\text{O}$  species, the application of the reaction mechanisms indentified in dry melt is questionable in the case of water-bearing melts.

Cylinders of crystal free glasses were exposed, at high temperature (and pressure), to atmospheres containing  $\text{H}_2\text{-H}_2\text{O-Ar-CO}_2\text{-CO}$ . The progression of a redox front within the glass was optically monitored and the associated chemical migrations were characterized using electron microprobe, infrared and Mössbauer spectroscopies. The advancement of the redox front was shown to be proportional to the square-root of time, revealing the overall reaction as a diffusion-limited process. Iso- $f\text{O}_2$  experiments performed with different gas mixtures,  $\text{CO}_2\text{-CO}$ ,  $\text{Ar-H}_2$ , and  $\text{CO}_2\text{-H}_2$ , have shown that the hydrogen fugacity,  $f\text{H}_2$ , rather than  $f\text{O}_2$  is the dominant parameter controlling the reaction rate. The  $f\text{H}_2$  dependence of the reaction rate

was then characterized in the range 0.02 to 70 bar of  $f\text{H}_2$ . The growth rate of the redox front, which is accompanied by changes in the quantity of reaction-derived OH-groups, was successfully fitted considering that the reduction rate is controlled by the migration through the melt of a free mobile species ( $\text{H}_2$ ) immobilized in the form of OH subsequent to reaction with ferric iron. The extremely weak temperature dependence of the reaction rate was shown to be consistent with the activation energy for molecular  $\text{H}_2$  migration in silicate melt (~40 kJ/mol). Furthermore, we extracted a solubility law for molecular  $\text{H}_2$  in silicate melts that matches well the results of previous studies. Probably due to its small size, we found that both solubility and mobility of  $\text{H}_2$  in melt is almost insensitive to the structure of the melt [8].

We therefore provide a model that allows the prediction of oxidation-reduction rates in the presence of hydrogen for a wide range of melt compositions. Comparisons with previous work elucidating the rate of redox exchange in dry systems allow us to anticipate the  $f\text{H}_2\text{-T}$  domains where different redox mechanisms may apply. We conclude that equilibration of redox potential in nature should be dominated by  $\text{H}_2$  transfer at a rate controlled by both  $\text{H}_2$  solubility and diffusion in melt. Therefore, changes in the redox state of magmas are intimately related to changes in the concentration of water-derived species. Several consequences of these findings are proposed.

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**HYDROTHERMAL SYSTEMS ON TERRESTRIAL PLANETS: LESSONS FROM EARTH.** R. T. Gregory<sup>1</sup> <sup>1</sup>Stable Isotope Laboratory, Department of Geological Sciences, SMU, PO Box 750395, Dallas TX 75275; bgregory@smu.edu

**Introduction:** Stable isotopic measurements have been instrumental in elucidating the role of fluid-rock interaction in the lithosphere of the Earth; e.g. [1]. Analyses of geothermal fluids [2] and subsurface formation waters [3] provide direct evidence of penetration of surface waters into the crust. Oxygen isotope determinations of whole rocks and their coexisting minerals, e.g. [4,5], provided evidence for the depth of penetration of hydrothermal fluids and mechanisms of isotopic exchange necessary to explain the variations of observed in the water studies. Earth, with water near its triple point at the surface and with silicates near their solidus in the mantle at the base of the lithosphere, provides tremendous opportunities for generating oxygen isotopic heterogeneities in the lithosphere.

**Isotopic Impact of Fluid Rock Interaction:** The temperature dependence of oxygen isotopic fractionations between silicates varies from approximately +40 ‰ at surface temperatures (e.g. quartz-water) to  $\approx -2$  ‰ (magma-water) at magmatic temperatures. The temperature dependence of the solid-water isotope fractionation along with the high thermal gradient at midocean ridges generates the conditions for exchange between dominant silicate (the mantle) and water (the ocean) reservoirs. The time scale for this exchange is approximately 100 Myr, e.g. [6]; this buffers the oxygen isotopic composition of the oceans. The isotopic composition of the ocean anchors the meteoric water cycle, which in turn determines the range of possible fractionations with the crust at near surface conditions. The net result is that the lithosphere exhibits a  $\approx 50$  ‰ spread in  $\delta^{18}\text{O}$  values; in contrast to homogeneous post-accretion, differentiated Earth-Moon system at +6 ‰.

**$\delta$ - $\delta$  Representation:** The natural coordinate system for representing stable isotopic variations is the  $\delta$ - $\delta$  plot that simultaneously portrays the effects of temperature and mass balance on stable isotope distributions. In a fluid + rock binary system, any natural system generates a spectrum of fluid compositions ranging from fluid-buffered to rock-buffered; this is controlled by the dimensionless ratio of the fluid flux rate to the reaction rate ( $u/k$ ). The primary controls on this critical ratio are permeability (for  $u$ ) and temperature (for  $k$ ). Mechanical limits on permeability at depth allow the preservation of surface-derived isotopic heterogeneities to great depths and for geologically long time scales. When  $u/k \ll 1$ , the fluid isotopic composi-

tion is buffered by the local host rocks on time scales of 1000's of years while mineral heterogeneities will persist for millions of years. Secondary phases grown in the presence of this buffered fluid will reflect isotopic equilibrium with the local fluid environment and exhibit non-equilibrium fractionations with the remaining partially-exchanged phases. The time scales for this type of fluid-rock interaction are comparable to time scales for assembly for meteoritic parent bodies.

**Implications for  $^{17}\text{O}$ - $^{18}\text{O}$  Plots.** Translating complete open system behavior into the  $\delta^{17}\text{O}$ - $\delta^{18}\text{O}$  coordinate system shows that exchange between a "terrestrial-like" oxygen reservoir and a low  $\Delta^{17}\text{O}$  reservoir generates an array of slope 1 for systems whose end members are initially far from isotopic equilibrium; this is similar to the observed chondritic arrays [e.g. 7].

For most achondrites, magmatic differentiation and subsolidus exchange generates arrays that follow mass dependent arrays whose isotopic ranges along the arrays are consistent with high-T exchange [e.g. 8]. Secondary carbonates in some CM2 chondrites exhibit behaviors consistent with an intermediate behavior, probably very locally-buffered, exhibiting 1) large fractionations between the carbonate phases and coexisting matrix and 2) approach to a mass dependent fractionation line while 3) exhibiting non-equilibrium, reversed  $\Delta^{18}\text{O}$  values between dolomite and calcite [9].

Extrapolation of these types of results to the hydrology of meteoritic parent bodies, e.g. [10], depends upon the phase diagram for water and whether liquid-water can survive where hydrostatic pressures would be well below 1 bar. The water vapor-liquid transition also would have important consequences for the evolution of the shallow crust of Mars.

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**Oxygen in martian meteorites: A review of results from mineral equilibria oxybarometers.** C. D. K. Herd<sup>1</sup>,  
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**Introduction:** Two oxybarometers based on mineral equilibria have been used to determine oxygen fugacity ( $fO_2$ ) in the martian meteorites: the Fe-Ti oxide and olivine-pyroxene-spinel (Ol-Px-Sp) methods. The details of these methods and a review of their application to martian basalts (i.e., basaltic and olivine-phyric shergottites) is provided in [1]. The purpose of this abstract is to summarize results for martian basalts (Table 1) and to provide details that elucidate the advantages and potential pitfalls of these methods.

**Fe-Ti oxides method:** This method is based on the compositions of co-existing titanomagnetite (spinel) and ilmenite. These are common accessory minerals in basaltic shergottites such as Shergotty, Zagami, Los Angeles, and QUE 94201.

Any thermodynamic model is limited by the data used in its construction. Such is the case with the Fe-Ti oxide oxybarometer models [2, 3] – significant deviation in composition of the oxides from “ideal” Fe-Ti endmembers results in greater uncertainty. As noted by [4, 5], its application to certain oxides is problematic. For example, in Dar al Gani 476, spinel contains up to 20 wt%  $Cr_2O_3$  and ilmenite 5 wt% MgO. The Ol-Px-Sp method (see below) presents a more suitable alternative in such cases [5].

Subsolidus diffusion presents an additional complication. Oxyexsolution of titanomagnetite results in lamellae of ilmenite in the spinel host, as seen in QUE 94201 [4], NWA 480 [6], and the Ti-rich rims of chromite in NWA 1110 [7] and Dhofar 019 [8], among others. Although the lamellae are typically less than 1  $\mu m$  in width, their presence results in increased uncertainty in  $fO_2$  (e.g., compare the range of  $fO_2$  for QUE 94201 with that of other samples in Table 1). Whether the oxyexsolution occurred as a result of an increase in  $fO_2$  (open-system) or under ambient  $fO_2$  (closed-system) conditions is unclear. Open-system conditions imply that the titanomagnetite in QUE 94201 has been oxidized; therefore, the Fe-Ti oxide results should be considered an upper limit on the  $fO_2$ .

**Ol-Px-Sp method:** This method is based on the compositions of co-existing olivine, pyroxene and Cr-spinel. These assemblages are common in the olivine-phyric shergottites such as DaG 476, SaU 005, Dhofar 019, NWA 1110 and Y980459. Careful petrographic observations are required to select equilibrium assemblages for  $fO_2$  calculation [7, 9]. In some cases,  $fO_2$  can be estimated for different generations of assemblages, allowing evaluation of  $fO_2$  changes with cooling.

**Table 1: Summary of  $fO_2$  results for martian basalts.**

Sample	T (°C)	$fO_2$ range <sup>a</sup>	Comments <sup>b</sup>
Zagami	756 – 816	-1.0 to -1.5	FeTi, [4]
Shergotty	759 – 793	-1.1 to -1.2	FeTi, [4]
QUE94201	624 – 794	-2.4 to -3.8	FeTi, [4]
Los Angeles	748 – 832	-1.0 to -1.6	FeTi, [4]
NWA 3171 <sup>c</sup>	761 – 782	-1.3 to -1.4	FeTi [10]
Y980459 <sup>c</sup>	1400 <sup>d</sup>	-2.7 to -3.5	OPS
Dhofar 019	1099	-3.7	OPS, [7, 9]
	650 – 800	-3.8 to -4.3	FeTi, [8]
EET79001B	712 – 848	-1.3 to -2.4	FeTi, [4]
EET79001A	794 – 1009	-1.1 to -1.9	FeTi, [4]
groundmass	730 – 925	-1.7 to -1.9	OPS, [7, 9]
EET79001A xenocrysts	854 – 982	-2.5 to -3.0	OPS, [7, 9]
DaG 476	774 – 1186	-1.9 to -3.3	OPS, [7, 9]
SaU 005	1017-1154	-3.0 to -3.8	OPS, [7, 9]
SaU 005 L <sup>e</sup>	1047-1093	-3.0 to -3.4	
NWA 1110	996 – 1063	-1.2 to -2.0	OPS, [7, 9]
NWA 1110 L <sup>e</sup>	766 – 836	-0.5 to 0.5	
ALH77005	1273	-2.6	OPS, [7]

Notes: <sup>a</sup> $fO_2$  relative to QFM [11]; <sup>b</sup>FeTi = Fe-Ti oxide method of [2], OPS = Ol-Px-Sp method [5, 9]; <sup>c</sup>preliminary results; <sup>d</sup>Estimate; <sup>e</sup>L = late assemblage [7, 9].

**Comparison of the methods:** The criticism that the results of these methods, especially Fe-Ti oxides, do not represent magmatic  $fO_2$  conditions has been addressed [4, 7]. In sum, the T- $fO_2$  trends recorded by either method indicate that  $fO_2$  changes very little with cooling and crystallization in most cases: the spread of estimates in a given sample run parallel to the QFM buffer in T- $fO_2$  space. The notable exceptions are EET 79001 lithology A and NWA 1110 (Table 1); in these cases, variations are attributable to processes in the magma [e.g., 7], as opposed to errors in  $fO_2$ .

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**NON-LINEAR FRACTIONATION OF OXYGEN ISOTOPES IMPLANTED IN LUNAR METAL GRAINS: SOLAR, LUNAR OR TERRESTRIAL ORIGIN?;** T. R. Ireland, P. Holden, M. Norman, and J. Clarke, Research School of Earth Sciences, The Australian National University, Canberra ACT 0200, Australia <Trevor.Ireland@anu.edu.au>

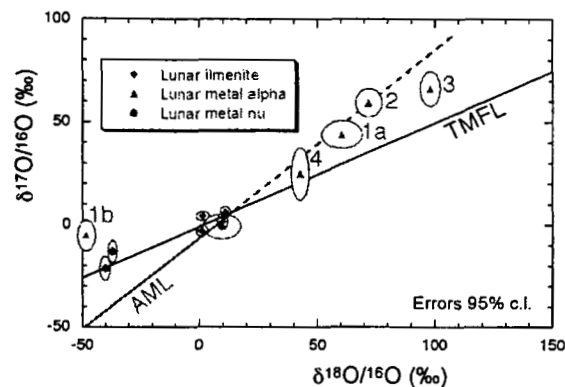
**Introduction:** The imminent return of the Genesis experiment motivated us to look for natural analogs. The occurrence of metal grains in lunar soil offers such a possibility. The metal, probably splash droplets from meteorite impacts, offer a robust medium with low intrinsic concentrations of oxygen. These grains have been exposed to surface conditions and effects, most notably to the solar wind for a much longer time than the Genesis materials and hence signals should be larger, making for easier analytical conditions.

**Analytical:** The analyses were carried out on SHRIMP II in multiple collection mode. A 1 nA Cs<sup>+</sup> beam was used to sputter oxide and metal grains and all samples were analyzed with a faraday cup for <sup>16</sup>O<sup>-</sup> and CDEM for <sup>17</sup>O<sup>-</sup> and <sup>18</sup>O<sup>-</sup>. Terrestrial magnetite and ilmenite analyses were interspersed with analyses of the metal grains. Preliminary results were presented previously [1].

**Results:** The results of the analyses are shown in Figure 1. One spherical grain (v) shows highly anomalous compositions. The most anomalous compositions are in the first analyses of the surface with progressively lower anomalies and <sup>16</sup>O<sup>-</sup> count rates as the ion beam sputters deeper into the grain. These compositions lie on a non-linear mass fractionation line of approximately unit slope with relative depletion of <sup>16</sup>O (or <sup>17</sup>O, <sup>18</sup>O enrichment) of up to 100 ‰. One analysis (1b) of grain v, and the analyses of another grain (v) are dominated by contamination (non-decaying depth profiles) and lie on or close to the terrestrial mass fractionation line at about -50 ‰. The lunar ilmenites are corrected for temporal variations in the counting system, but this correction is highly correlated with total counts, and it would not produce the magnitude of the effects measured.

**Discussion:** The lunar metal grains provide an isotopic composition that has not been seen previously beyond the terrestrial atmosphere. Is this the composition of solar wind, is it a surface effect on the Moon, can Earth atmosphere oxygen interact with the Moon?

Decaying depth profiles make it tempting to consider that the <sup>16</sup>O-depleted composition is that of the solar wind. Then the question will remain as to whether this is the composition of the Sun, or a composition formed by the processes responsible for solar wind acceleration.



**Figure 1.** Oxygen isotopic compositions in lunar metal grains. Grain alpha has a highly anomalous surface composition depleted in <sup>16</sup>O relative to terrestrial (+lunar). Analysis 1b and grain v are dominated by contamination.

Isotopic mass fractionation is well known from lunar soils but this is mass dependent (linear) mass fractionation enriching the heavy isotopes in the grain surfaces as a result of grain sputtering [2].

The extreme depletion of <sup>16</sup>O (or <sup>17</sup>O, <sup>18</sup>O enrichment) in the lunar metal is a factor of two larger than the CWAS samples of Earth's stratosphere (e.g. [3]). Coincidentally, it has been postulated that Earth atmosphere components (N, noble gases) could be transported (as ions) to the Moon when the geomagnetic field was weaker during the early Earth [4].

The metal grains lack intrinsic oxygen requiring that any oxygen be surface related. At this stage, it is unclear whether the oxygen is implanted below the surface (as for solar wind) or present at the surface. Resolution of this issue will help establish the source of this exotic oxygen. The Genesis experiment will resolve the issue of a solar origin. If Genesis returns a composition markedly different than the composition measured here (viz. close to refractory inclusions or meteorites/terrestrial planets), then a hitherto unknown mechanism is responsible for a high degree of non-linear O isotope fractionation.

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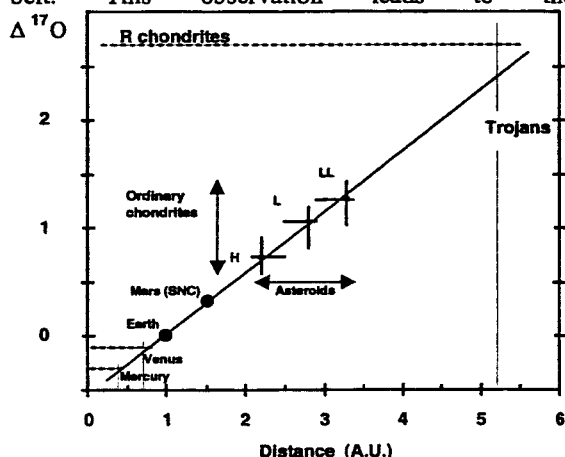
# ISOTOPIC ZONING IN THE INNER SOLAR SYSTEM. A. Jambon<sup>1</sup>, Laboratoire MAGIE, Université Pierre et Maris Curie Case 110, 4 place Jussieu, 75252 Paris cedex 05, France. jambon@ccr.jussieu.fr

**Introduction:** The main lines of meteorite classification rest upon chemical criteria. Primitive meteorites or chondrites derive their composition directly from the solar nebula without differentiation processes in their parent body (e.g. no core extraction). Chondrites are distinguished from differentiated meteorites (achondrites and siderites). More detailed studies of chondrites showed they could be separated into a number of classes, the most effective criterion for that being the oxidation state of iron, which can be either combined as a metal alloy (with Ni) or with sulfur or oxygen. In this latter case it enters the constitution of Fe-Mg silicates, like olivine. The following major groups are distinguished: carbonaceous chondrites wherein Fe is completely oxidized or nearly so, ordinary chondrites which are intermediate and enstatite chondrites in which Fe is not combined to oxygen. These wide groups are further divided into classes using more subtle criteria, specific to each group. The most abundant meteorites by far, are the ordinary chondrites. Enstatite chondrites are least frequent but statistical considerations lead to conflicting views: If one class is poorly populated, one may argue that it is a curiosity, not an important one. Conversely one can say that this results from their great success in forming larger parent bodies and their study is therefore of utmost importance to the understanding of planetary bodies. According to this view, ordinary chondrites are expected to stem from the main asteroid belts. Accretion in this region has been highly perturbed by the vicinity of Jupiter so that no massive planet could emerge. Chondrites from this region can therefore be viewed as leftover from the planetary formation.

This discussion is supported by prejudices on the way the solar system evolved and planets formed; it is established on chemical and mineralogical criteria. For a few decades, oxygen isotopes have been used and confirmed the rationality of this classification since a new criterion independent from the chemical composition permitted to separate the same classes but the rationale behind it is not well understood.

**Facts:** After a rapid review of relevant isotopic data [1-4], especially the new data on achondrites [1,2], a strong correlation of  $\Delta^{17}\text{O}$  with distance from the sun appears. Zoning of the present day solar system is established and discussed. Oxygen isotopic compositions are fundamental data which permit to establish that the primitive solar system was isotopically zoned as a result of binary mixing. This is still visible in the present day planetary

compositions from Mercury to Mars and the asteroid belt. This observation leads to the



question of how did this zoning originate? The other question is how do carbonaceous chondrites fit in this picture?

**Conclusions:** According to this solar system zonation model we have to admit that our speculations on parent bodies of achondrites have to be revised: HED are from Mercury and angrites from Venus.

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# **REDOX CONDITIONS ON SMALL BODIES.** (john.h.jones1@jsc.nasa.gov).

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**The Eucrite Parent Body (4 Vesta).** The eucrites are basalts that contain ~18 wt% FeO and contain trace metal. The eucrites are very depleted in siderophile elements, so it appears that the source regions of these basalts once equilibrated with Fe-Ni metal [1]. Therefore, it is of interest to ask what  $f_{O_2}$  is required to precipitate metal from a liquid of eucrite composition. Or in other words, what  $f_{O_2}$  did eucrites form under? This  $f_{O_2}$  has been determined experimentally by [2] and was found to be IW-1. Therefore, eucrites formed at about IW-1. In addition, it is interesting to note that assuming  $X_{FeO} = a_{FeO}$  allows calculation of eucrite  $f_{O_2}$  (assuming equilibrium with Fe metal). This calculation yields the same result as the experiments to within ~0.25 log units, reinforcing this result.

Approaching this problem a third way, Jurewicz et al. [3] noted that partial melts of the Murchison (CM) chondrite at 1180-1200°C and IW-1 were virtually identical in their major element concentrations to those of eucrites.

Thus, several lines of evidence conspire to convince us that eucrites formed near IW-1. Further, we anticipate that basalts having ~18 wt.% FeO and coming from planetary mantles that experienced core formation should also have  $f_{O_2}$ 's near IW-1. This is true for the Moon [4] and now appears to be approximately true for Mars [5].

**Ordinary Chondrites.** In addition to experiments on eucrites themselves, we may approach the problem from another direction. Larimer [6] noted that an assemblage of olivine, low-Ca pyroxene and metal can be used to evaluate redox conditions:



a variant of the QFI buffer, which is about IW-0.5. To the extent that FeO does not fractionate greatly between olivine and pyroxene and that the Fe-Ni metal is mostly Fe, then the above reaction will also not stray greatly from the QFI buffer, as long as non-idealities are not large. Therefore, we anticipate that ordinary chondrites and their achondritic relatives, lodranites and acapulcoites, will also have redox states in the vicinity of IW-0.5 to IW-1.

Thus, from our experience with eucrites, lunar mare basalts, and ordinary chondrites, a picture emerges that small bodies whose mantles initially contained olivine, low-Ca pyroxene and Fe-Ni metal will, upon partial melting, produce basalts that contain ~18

wt.% FeO and that this process will take place at oxygen fugacities near IW-1. Therefore, ~18 wt% FeO in a basalt is an easily recognizable signature of a particular  $f_{O_2}$ .

**Exceptions to the Rule.** Not all chondrites and asteroids are as reduced as ordinary. The enstatite chondrites and their achondritic associates (aubrites) are much more reduced and contain little or no FeO. And some bodies are more oxidized than the ordinary chondrites. This is emphasized by the observation that some asteroids have a small  $Fe^{3+}$  absorption feature [7]. Do we see any igneous meteorites that appear to have come from more oxidized bodies. As a matter of fact we do.

One class of igneous meteorites that does not easily fit into normal categories is the angrites. They are critically silica undersaturated and have unusual mineralogies. Experimental melts of Allende (CV) performed at IW+1 and IW+2 are the best matches to the most primitive angrites [8]. So it appears that we now have samples from oxidized mantles other than the Earth's.

Even though the angrites are more oxidized than the eucrites, their source region probably contained metal. We infer this because siderophile elements are depleted in the angrites [e.g., 9]. The reason metal can remain stable above the IW buffer is because of the presence of Ni. Since the Ni-NiO buffer is about 4.5 log units above IW, Ni can expand the Fe-Ni metal stability field; and Ni-rich metal is observed in Angritos Reis. Thus, the uncommon mineralogies observed in the angrites is directly attributable to the redox conditions during the partial melting of the angrite source regions.

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**DETERMINING THE OXYGEN FUGACITY OF LUNAR PYROCLASTIC GLASSES USING VANADIUM VALENCE-AN UPDATE** J.M. Karner<sup>1</sup> (jkarner@unm.edu), S.R. Sutton<sup>2,3</sup>, J.J. Papike<sup>1</sup>, C.K. Shearer<sup>1</sup>, J.H. Jones<sup>4</sup>, and M. Newville<sup>3</sup>. <sup>1</sup>Institute of Meteoritics, Dept. of Earth and Planetary Sciences, University of New Mexico, Albuquerque, NM 87131-1126; <sup>2</sup>Dept. of Geophysical Sciences and <sup>3</sup>Consortium for Advanced Radiation Sources, University of Chicago, Chicago, IL 60637, <sup>4</sup>SR NASA/JSC, Houston, TX 77058

**INTRODUCTION** We have been developing an oxygen barometer based on the valence state of V ( $V^{2+}$ ,  $V^{3+}$ ,  $V^{4+}$ , and  $V^{5+}$ ) in solar system basaltic glasses. The V valence is determined by synchrotron micro x-ray absorption near edge structure (XANES), which uses x-ray absorption associated with core-electronic transitions (absorption edges) to reveal a pre-edge peak whose intensity is directly proportional to the valence state of an element [1]. XANES has advantages over other techniques that determine elemental valence because measurements can be made non-destructively in air and *in situ* on conventional thin sections at a micrometer spatial resolution with elemental sensitivities of ~100 ppm. Recent results show that  $fO_2$  values derived from the V valence technique are consistent with  $fO_2$  estimates determined by other techniques for materials that crystallized above the IW buffer [2]. The  $fO_2$ 's determined by V valence (IW-3.8 to IW-2) for the lunar pyroclastic glasses, however, are on the order of 1 to 2.8 log units below previous estimates [3,4]. Furthermore, the calculated  $fO_2$ 's decrease with increasing  $TiO_2$  contents from the A17 VLT to the A17 Orange glasses. In order to investigate these results further, we have synthesized lunar green and orange glasses and examined them by XANES.

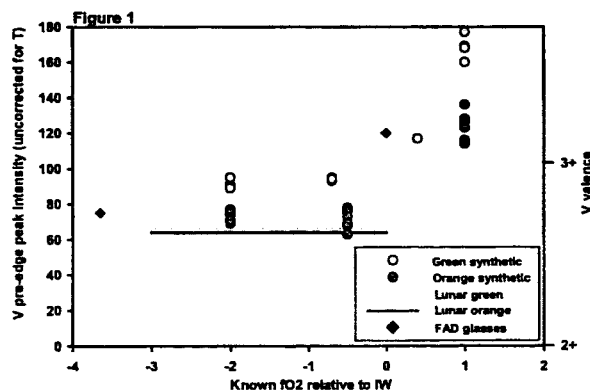
**EXPERIMENTAL** Lunar green and orange glass compositions were synthesized at several different  $fO_2$  conditions in the 1 atm gas-mixing furnaces at NASA JSC. The starting compositions were Apollo 15 Green C, containing about 16 wt.% FeO, 0.2 wt.%  $TiO_2$ , 0.6 wt.%  $Cr_2O_3$ , and Apollo 17 Orange, containing 26 wt.% FeO, 9 wt.%  $TiO_2$ , 0.7 wt.%  $Cr_2O_3$ ; both compositions were doped with 5000 ppm V. The glasses were produced by drop quenching into water after equilibrating at imposed  $fO_2$  conditions of approximately IW+1, IW, IW-1, and IW-2 at 1430 °C. The glasses were then examined by electron microbeam techniques and found to be homogenous and free of crystals, although there was systematic FeO loss with decreasing  $fO_2$ , presumably to the Re-wire used to suspend the samples in the furnace.

**RESULTS AND DISCUSSION** Figure 1 shows the V pre-edge peak intensities for synthetic glasses against the  $fO_2$  values at which they were produced, as well as the intensities for the natural lunar green and orange glasses (lines). The plot shows a plateauing of V pre-edge peak intensity (i.e. V valence) independent of  $fO_2$  below approximately IW-0.5. The plateauing, or

stabilization of  $V^{2+}/V^{3+}$  suggests it may be difficult to quench  $V^{2+}$ , an effect that has been documented for  $Cr^{2+}$  in basaltic glasses [5]. The inability to quench reduced Cr in glasses is attributed to the oxidation of  $Cr^{2+}$  to  $Cr^{3+}$  on cooling in the presence of  $Fe^{3+}$  by electron exchange. Here we could be seeing the oxidation of  $V^{2+}$  to  $V^{3+}$  by either  $Cr^{3+}$  or  $Ti^{4+}$ . Another explanation could be that  $V^{2+}$  does not exist in our samples, and the transition from  $V^{3+}$  to  $V^{2+}$  occurs at much lower  $fO_2$  conditions than previously expected. Figure 1 also shows the effect of composition on V valence. The orange synthetic glasses (9 wt.%  $TiO_2$ ) show a lower valence than the green synthetic glasses (0.2 wt.%  $TiO_2$ ), even though they were produced at the same  $fO_2$ . This compositional effect is not seen in the natural orange and green glasses however, and leads us to believe that doping the green synthetic mix with V resulted in a greatly increased V/Ti ratio compared with the natural samples, and in turn this has affected the V valence. The final observation from Figure 1 is that the lunar green and orange glasses plot at essentially the same V valence, which also corresponds to the V valence of the IW-0.7 and IW-2 orange synthetic samples. From these observations, we conclude that our best estimate of the  $fO_2$  for the lunar glass beads is IW-1, with an uncertainty of about 1 log unit.

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**ACKNOWLEDGEMENTS** We thank L. Le for her expert help in the gas-mixing furnace lab at NASA JSC. This work supported by a NASA Cosmochemistry grant to JJP. GSECARS is supported by the NSF, U.S. DOE, W.M. Keck Foundation, USDA, and the State of Illinois.



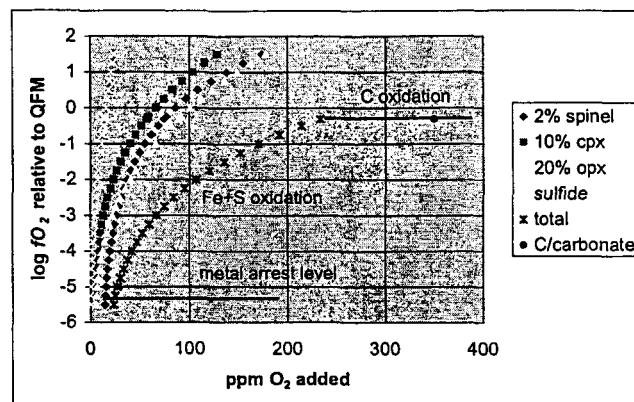
**MANTLE REDOX EVOLUTION AND THE RISE OF ATMOSPHERIC O<sub>2</sub>.** J. F. Kasting, Department of Geosciences, 443 Deike, Penn State University, University Park, PA 16802; kasting@essc.psu.edu.

Why did atmospheric O<sub>2</sub> rise around 2.3 Ga [1,2] when photosynthetic cyanobacteria appear to have arisen at least 400 m.y. earlier [3]? Either cyanobacterial productivity was lower for some reason during the Archean, or else the volcanic sink for O<sub>2</sub> must have been larger. The relative constancy of the  $\delta^{13}\text{C}$  values of carbonates at ~0‰ both before and after the initial rise of O<sub>2</sub> implies that organic carbon burial rates did not change and, hence, that the volcanic sink for O<sub>2</sub> must have decreased with time. Kasting et al. [4] suggested that this happened because the upper mantle became progressively oxidized during the Archean as hydrogen escaped to space. The hydrogen came from water originally, so this process would have oxidized the Earth. In their model, it was Earth's upper mantle that was oxidized by subduction of water and carbonates, followed by outgassing of H<sub>2</sub> and CO. Subduction of ferric iron may also have been important [5]. As the upper mantle became more oxidized, the volcanic gases would have become less reduced, until eventually they were overwhelmed by photosynthetically produced O<sub>2</sub>.

This hypothesis, while attractive in many respects, is in apparent disagreement with observations. Data on the Cr and V content of ancient basalts and komatiites [6-8] indicate that upper mantle  $f\text{O}_2$  has changed very little since at least 3.5 Ga. A recent reanalysis of volcanic gas oxidation states by Holland [9] shows that only a small change (<1 log unit) in  $f\text{O}_2$  may be required in order to get the atmospheric oxidation state to flip, but even this small change may be ruled out. Thus, the question of why atmospheric O<sub>2</sub> rose when it did remains a mystery.

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**Fig. 1** Diagram showing how many ppm (by weight) of O<sub>2</sub> must be added to the upper mantle in order to increase its oxidation state from iron-wüstite (IW) to quartz-fayalite-magnetite (QFM). This estimate assumes 10<sup>24</sup> kg of material above 700 km depth and ~6 wt. percent Fe. The total O<sub>2</sub> added is ~7×10<sup>21</sup> mol. By comparison, the present rate of volcanic input of H<sub>2</sub> is 5×10<sup>12</sup> mol/yr, and the Archean volcanic input rate was probably several times higher. Escape of a significant fraction of this H<sub>2</sub> prior to 2.3 Ga could have led to progressive mantle oxidation.

## Variation of Kd for Fe-Mg Exchange Between Olivine and Melt for Compositions Ranging from Alkaline Basalt to Rhyolite

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Analysis of more than 200 olivine-melt pairs in terms of Fe-Mg exchange between olivine and coexisting melt indicates that Kd varies with bulk composition and oxygen fugacity. For tholeiitic basalts Kd value is  $0.3 \pm 0.03$ ; however, as the composition changes from tholeiitic to alkaline the Kd decreases to as low as 0.18. On the other end of the compositional spectrum as the silica content of melts increase to rhyolitic composition Kd increases up to 0.68.

Our calculations of Kd using Sack et al. (1980), Kilinc et al. (1983) and Kress and Carmichael (1988) equations relating Fe<sup>3</sup>/Fe<sup>2</sup> to temperature, oxygen fugacity and compositional parameters shows that Kd is a function of composition. Using S/SCAM as the differentiation index a third degree polynomial equation value of Kd can be calculated for any bulk composition.

$$\ln K_D = 24.937 \cdot (S/SCAM)^3 - 27.769 \cdot (S/SCAM)^2 + 9.9783 \cdot (S/SCAM) - 2.4363$$

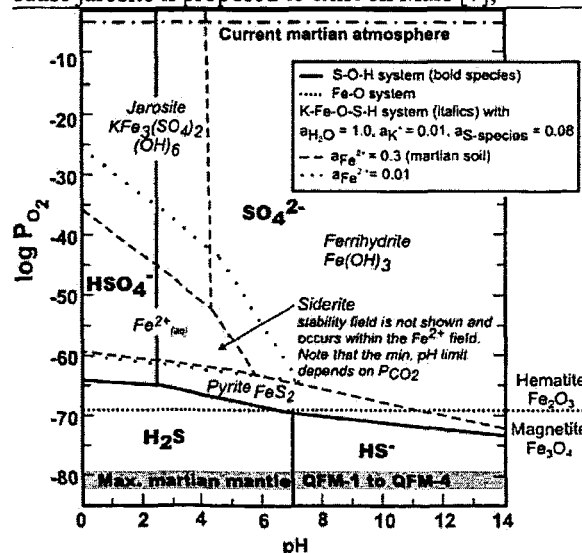
# **DETERMINING THE PARTIAL PRESSURE OF OXYGEN ( $P_{O_2}$ ) IN SOLUTIONS ON MARS.** P. L. King (Dept. Earth Sciences, Rm. 128A, B&G Bldg., University of Western Ontario, London ON N6A 5B7 Canada).

The current martian atmosphere has  $\log(P_{O_2}) = -5$ , but martian mantle estimates are below the quartz-fayalite-magnetite (QFM) buffer ([1,2]; recalculated as  $\log(P_{O_2}) < -79$  at 25°C using data from [3]). Also, it is likely that early Mars had relatively low  $P_{O_2}$  conditions, analogous with those proposed for the early Earth [4]. Here, I examine the martian  $P_{O_2}$  evolution using phase equilibria,  $S^{2-}/S^{6+}$  and  $Fe^{3+}/Fe^{2+}$  minerals or species in surface solutions on Mars.

## **$P_{O_2}$ of martian solutions**

The primordial solutions on Mars likely contained C-O-H-S-N-halogen species (similar to Earth [4]). Such reactive solutions may have leached the martian surface materials (sulfides-Fe-Mg minerals-plagioclase-glass) to produce saline solutions [5]. Since pyrite is the most easily leached mineral, we can model the leaching solutions in the Fe-O-S-H system. At low  $P_{O_2}$   $H_2S$  and  $HS^-$ -bearing solutions are predicted as a function of pH (Fig.). It is probable that  $\log(P_{O_2}) > -69$  because  $Fe^{3+}$  (hydrous) oxides, (e.g. hematite) are found on the martian surface [6] (Fig.).

To further constrain  $P_{O_2}$  on the martian surface it is possible to examine the stability of phases in the K-Fe-C-O-S-H system. This system is chosen because jarosite is proposed to exist on Mars [7],



Stability limits of Fe-bearing phases relative to pH and  $P_{O_2}$  in the K-Fe-O-S-H system at 25 °C and  $\sim 10^5$  Pa. At lower martian temperatures the  $P_{O_2}$  values will be lowered [9,15] and there may be effects due to the anion content [15], therefore the data should be assessed with reference to displacement from the buffer reactions.

siderite and ferrihydrite are observed in martian meteorites [8] (where ferrihydrite is used as a proxy for goethite and magnetite following [9]).

The figure shows stability limits for model martian surface compositions calculated using the Viking and Pathfinder soils [10-12] ( $a_{K^+}=0.01$ ,  $a_{S-species}=0.08$ ,  $a_{Fe^{2+}}=0.3$ ), using equilibrium constants from [13-14], assuming that activity coefficients and the activity of water are unity (see [9] and [15] for a discussion of assumptions).

At near-neutral to acidic conditions, pyrite weathers to either  $Fe^{2+}_{aq}$  or siderite (Fig.). Siderite stability depends on  $P_{CO_2}$ , with a lower limit of pH $\sim$ 3.9 for  $P_{CO_2} = 2$  and pH $\sim$ 4.7 for  $P_{CO_2} = 0.05$ . If conditions are acidic and  $P_{O_2}$  is higher then jarosite precipitates. If K is a limiting component, then other ferric hydroxy-sulfate minerals may precipitate. If jarosite is present on the martian surface, then the solutions contain  $SO_4^{2-}$  or  $HSO_4^-$ , dependent on pH. If conditions are near-neutral to basic, then ferrihydrite (or other Fe-(hydr)oxides) precipitate. If  $a_{Fe^{2+}}$  is lower (due to precipitation of Fe-minerals), then higher  $P_{O_2}$  is required to form jarosite and ferrihydrite (Fig.).

## **Possible method to increase $P_{O_2}$ on Mars**

On Mars,  $H_2$ -loss is indicated by the high D/H value of the martian atmosphere relative to the martian mantle [16]. Hydrogen-loss may drive up oxygen fugacity [17] via reactions such as dehydrogenation of the atmosphere ( $H_2O = H_2 + 0.5O_2$ ), which in turn may promote oxidation of Fe in solids (e.g., martian amphiboles [18]).

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**THE INFLUENCE OF OXYGEN ENVIRONMENT ON KINETIC PROPERTIES OF SILICATE ROCKS AND MINERALS.** D. L. Kohlstedt<sup>1</sup>, S. Hier-Majumder<sup>1</sup>, and S. J. Mackwell, <sup>1</sup>Department of Geology and Geophysics, University of Minnesota, Pillsbury Hall, Minneapolis, MN 55455, <sup>2</sup>Lunar and Planetary Institute, 3600 Bay Area Boulevard, Houston, TX 77058.

**Abstract:** The oxygen content in a geologic environment, expressed as oxygen partial pressure or oxygen fugacity, has a direct effect on the kinetic properties of rocks composed of minerals that contain a significant concentration of transition metal cations. In this context, the most extensively studied mineral is Fe-Mg olivine. Experimental investigations demonstrated that the rates of cation diffusion, electrical conductivity, and creep all increase systematically with increasing oxygen partial pressure. The measured dependencies of such physical properties on oxygen partial pressure provide insight into the mechanisms by which ionic and electronic transport proceed as well as constraints on the variation of these properties from one environment to the next.

Investigations of cation diffusion in olivine all yield a power law relation between diffusivity,  $D_{Me}$ , and oxygen partial pressure,  $p_{O_2}$ , with  $D_{Me}$  increasing as  $p_{O_2}$  to the 1/7 to 1/5 power [1-4]. Related thermogravimetry experiments yield the same dependence for cation vacancy concentration,  $X_V$ , on  $p_{O_2}$  [5,6]. Therefore, the authors of [3] have concluded that cation diffusion takes place by a vacancy mechanism, since  $D_{Me}$  is directly expressed in terms of the cation vacancy concentration and the vacancy diffusivity,  $D_V$ , through the relation  $D_{Me} = X_V \times D_V$ .

Measurements of the dependence of electrical conductivity on  $p_{O_2}$  in olivine provide related constraints on the mechanisms of charge transport. In the case of electrical conductivity, the analysis is somewhat more complicated than for cation diffusion because multiple electronic and ionic species can contribute. For olivine, a transition occurs from conduction primarily by electron holes (polarons) below 1100-1300°C to conduction by octahedral cations at higher temperatures [7-8]. Again, a key observation in identifying the mechanism of electrical conduction is the dependence of conductivity on oxygen fugacity, here combined with the activation energy.

Finally, studies of creep of olivine single crystals reveal a clear increase in creep rate with increasing  $p_{O_2}$  [10,11]. Because creep involves not only ionic diffusion but also dislocation motion, the results are more difficult to interpret in terms of fundamental mechanisms. The dependence of creep rate on  $p_{O_2}$  and temperature is more complex than in the case of cation diffusion or electrical conductivity. Both the  $p_{O_2}$  dependence and the  $T$  dependence of creep rate varying with the slip system activated as well as the ranges of

$p_{O_2}$  and temperature investigated. The dislocation microstructure also changes from one  $p_{O_2}$ - $T$  regime to the next, indicating transitions from glide-dominated to climb-dominated to cross slip-dominated dislocation processes [12].

Each of these kinetic properties plays an important role in mantle processes of the terrestrial planets. Cation diffusion controls the rate of chemical exchange and degree of zoning observed in olivine grains transported in basaltic magmas. Magnetotelluric observations provide constraints on the temperature distribution and composition of Earth's deep interior. Viscosity is a critical parameter for understanding convection in the mantle. While variations in oxygen fugacity produce only moderate changes in these important physical properties, analysis of the dependence of these properties on oxygen partial pressure provide critical insights into the fundamental mechanisms of transport. With this basis, a robust physical framework can be developed for extrapolating kinetic properties from the thermodynamic conditions imposed in laboratory experiments to those experienced by rocks in the mantle.

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# **REDOX EVOLUTION OF MAGMATIC SYSTEMS.** V.C. Kress, Earth and Space Sciences, University of Washington, Box 351310, Seattle, WA, 98195. kress@u.washington.edu

**Introduction:** Iron is the most abundant of the elements that exist in multiple redox states under typical terrestrial planetary conditions. Fe can exist in ferric, ferrous and metallic states under planetary conditions in percent to tens of percent concentrations. For this reason, iron-bearing phases will tend to be the principle buffers of redox variation in the terrestrial planets. Because of the relatively low chemical diffusivity of oxygen in solid phases, transfer and modification of relative redox potential in planetary bodies is primarily mediated by a melt or vapor phase [e.g. 1].

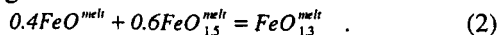
**Redox chemistry in silicate melts:** To a first approximation, ferric-ferrous equilibrium in silicate melts can be represented by the equation:

$$\ln \left( \frac{X_{\text{Fe}_2\text{O}_3}}{X_{\text{FeO}}} \right) = a \ln(f_{\text{O}_2}) + \frac{b}{T} + c + \sum X_i d_i \quad (1)$$

[2], where a, b, c and d's are empirically determined variables. Eq. 1 resembles a thermodynamic form, but differs in several important respects. Despite its thermodynamic shortcomings, Eq 1 has repeatedly been found to be the simplest functional form to adequately represent Fe-redox chemistry at 1 bar pressure in a remarkable variety of silicate melts.

Kress and Carmichael [3] used one-bar volume and compressibility data to extend Eq. 1 to allow calculation of redox equilibrium as a function of pressure. The resulting model suggested that a closed-system silicate melt at fixed redox state (closed system) will define an oxygen fugacity that roughly parallels solid oxygen buffers, such as the FMQ, as a function of both pressure and temperature. This would imply that adiabatically rising melts should not change their relative oxidation state unless they interact chemically with a contrasting redox reservoir.

[3] also pointed out that the apparently non-thermodynamic behavior of the Fe-redox behavior can be explained simply if one assumes that ferric and ferrous iron react to form an associated melt species by the homogeneous reaction:



The possible presence of such a mixed-valence melt species in silicate melts has been independently suggested based on spectroscopic data [4][5].

One bar experimental redox data suggests an equilibrium constant for reaction 2 of 0.4. a recent re-analysis of available silicate liquid density data [6] suggest that the volume of reaction for reaction 2 is not zero, as was assumed by [3], but must be on the order of -2.2 cc/mole. A non-zero  $\Delta V$  for reaction 2 implies

that the equilibrium constant is not independent of pressure.

A negative  $\Delta V$  for reaction 2 makes the predicted oxygen fugacity of an ascending closed-system melt parallel fugacities defined by typical solid oxygen buffers more closely than earlier models had suggested. This amplifies our previous conclusion that the relative redox state of silicate melts will reflect that of the host they most recently interacted with chemically.

Formation of an associated mixed-valence iron species will have significant effect on the activity coefficient of ferrous and ferric iron in silicate melts. At one-bar pressure, reaction 2 is responsible for decreasing the response of ferric/ferrous ratio in silicate melt to variations in oxygen fugacity relative to the effect expected if mixing were ideal. The negative volume of reaction for reaction 2 suggests that the slope of this response will decrease still further with increasing pressure. With increasing pressure, this volume term will decrease the activity coefficients for both ferrous and ferric components in the silicate melt.

**Sulfide phases:** Though sulfur is present in much lower concentrations than iron in the silicate Earth. Nevertheless, the large oxidation state change between sulfide ( $\text{S}^{2-}$ ), and sulfate ( $\text{S}^{6+}$ ) along with the fact that sulfur is important in solid, liquid and vapor phases leads to a disproportionately large influence of sulfur-bearing phases on redox chemistry in mantle and crustal systems. Because sulfur complexes with hydrogen, oxygen and carbon in the vapor phase, and with iron in the sulfide liquid and solid phases, the chemistry of sulfur in terrestrial planets is intimately tied to redox chemistry in subtle and complicated ways. Most experiments suggest that the solubility of sulfur in silicate melts decreases with increasing depth [e.g. 7]. This experimental pressure/solubility trend may be an oversimplification of the behavior of sulfur in natural magmatic systems.

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**THE CONSTANCY OF UPPER MANTLE  $fO_2$  THROUGH TIME INFERRED FROM V/SC RATIOS IN BASALTS: IMPLICATIONS FOR THE RISE IN ATMOSPHERIC  $O_2$ :** <sup>1</sup>Zhengxue Li, <sup>2</sup>Cin-Ty Aeolus Lee, [zxli@rice.edu](mailto:zxli@rice.edu), [ctlee@rice.edu](mailto:ctlee@rice.edu), Department of Earth Science, MS-126, Rice University, 6100 Main St., Houston, TX 77005

Understanding how the oxidation state of the Earth's mantle has evolved through time is critical to placing constraints on the timescales and nature of various planetary differentiation processes, such as core-mantle segregation, silicate differentiation, and atmospheric evolution. However, the secular evolution of the  $fO_2$  of the Earth's mantle is still not fully constrained because of the difficulties in obtaining direct measurements of the mantle through time. One approach is to use mantle xenoliths, but xenoliths are limited in space and time. Another approach is to measure the  $fO_2$  of basaltic lavas. Unfortunately, post-eruptive alteration and magmatic differentiation (e.g., fractional crystallization, degassing, and crustal assimilation) can change the  $fO_2$  of the magma during ascent. Approaches that use  $O_2$  thermobarometry [1] or use redox-sensitive elements to track fractional crystallization [2] yield only post-emplacement  $fO_2$ 's. An independent approach is to use the coupled systematics of V and Sc in primitive basalts. V and Sc are more similar to each other in partitioning behavior than to most other elements, but, in detail, V is redox-sensitive and Sc is not. Therefore, the V/Sc of primary magmas is to a large extent controlled by the  $fO_2$  during partial melting. Because V and Sc are not volatile and not highly enriched in continental crust, the magma remains largely closed to V and Sc during ascent. In addition, fractional crystallization of olivine cannot significantly change the V/Sc of the parent magma because V and Sc are highly incompatible in olivine. Thus, the V/Sc of basalts may be able to "see through" magmatic differentiation processes. V/Sc also provides a better redox-recorder than V alone because the latter suffers from dilution effects due to different degrees of partial melting. In order to describe the relationship between V/Sc and  $fO_2$ , we constructed a melting model to simulate the V and Sc distribution between solid residues and melts for different  $fO_2$  settings. We compiled V and Sc data for MORBs and Archean basalts (up to 3.5 Gy ago). The effects of fractional crystallization of clinopyroxene are minimized by filtering out samples with  $MgO < 8$  wt.%. The MgO-filtered data are plotted against  $1/Na$ , which is a proxy for degree of melting-F (Fig. 1). We assume that the average F is ~10% and thus use the V/Sc- $fO_2$  contours at F = 10% from our melting model to constrain the  $fO_2$  for modern and Archean basaltic magmas. The V/Sc of primitive MORBs average  $6.74 \pm 1.11$ , which constrains the  $fO_2$  of modern mantle to  $-0.2 \pm 0.5$  log units below the fayalite-magnetite-quartz (FMQ)

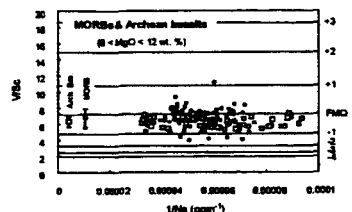


Figure 1. V/Sc vs  $1/Na$  for MORBs and Archean basalts.

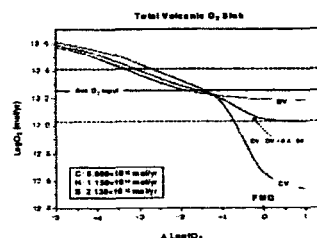


Figure 2. Modern volcanic  $O_2$  sink and  $O_2$  production.

buffer. This falls in the  $fO_2$  range for abyssal peridotites estimated using thermobarometric means ( $-2.5$  to  $+0.5$  log units from FMQ) [3], but is better constrained. Archean basalts have identical V/Sc ( $6.34 \pm 0.62$ ), indicating that the  $fO_2$  of their mantle source is identical to that of modern convecting mantle to within  $\pm 0.25$  log units. These new constraints represent an improvement on studies using V alone, which constrain the  $fO_2$  of Archean and modern mantles to be identical, but only to within  $\pm 1$  log unit [2, 4]. This places tight constraints on any planetary differentiation hypotheses involving  $fO_2$ -sensitive processes. For example, this rules out the possibility of secular changes in mantle  $fO_2$  as the cause for the rise in atmospheric  $O_2$  on Earth at 2.3 Gy [5]; [6]. In this context, we have revisited the role of volcanic degassing in modulating the levels of atmospheric  $O_2$  (Fig. 2). It can be seen that decreasing the volcanic  $O_2$  sink or increasing the  $O_2$  production can lead to a transition from an oxygen-poor to rich atmosphere. Alternatively, there may have been additional  $O_2$  sinks which gradually disappeared in the Phanerozoic.

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**NITROGEN SOLUBILITY IN BASALTIC MELT. EFFECTS OF OXYGEN FUGACITY, MELT COMPOSITION AND GAS SPECIATION.** G. Libourel<sup>1,2</sup>, B. Marty<sup>1,2</sup>, F. Humbert<sup>3</sup> and E. Gayer<sup>1</sup>. <sup>1</sup> CRPG, CNRS-EPR2300, BP20, 54501 Vandoeuvre-les-Nancy, France. <sup>2</sup> ENSG-INPL, BP40, 54501 Vandoeuvre-les-Nancy, France, <sup>3</sup> CFC-DAUM, 54112 Vannes le Chatel, France [libou@crpg.cnrs-nancy.fr](mailto:libou@crpg.cnrs-nancy.fr)

**Introduction:** Nitrogen is a major forming element of the Earth's atmosphere and one of the key elements of the biological evolution. Knowledge of its (elemental or isotopic) behavior is therefore of prime importance to understand and quantify processes which might have controlled the exchange of nitrogen between the mantle and the atmosphere through time. However in contrast to rare gases, mechanisms governing the incorporation of nitrogen in basaltic melts are not well documented.

**Experimental:** In order to provide much needed constraints, we have developed a combined experimental and analytical approach to measure nitrogen solubility in silicate melts. Equilibration were performed at one atmosphere and at 1425°C over a large range of oxygen fugacity controlled by mixtures of gases belonging to either [C-N-O] or [C-N-O-H] vapor systems. Nitrogen contents in equilibrated samples were measured using a technique based on CO<sub>2</sub> laser extraction in high vacuum line and static vacuum mass spectrometry and N speciation by FTIR measurements on selected N-bearing glass samples.

**Oxygen fugacity:** Over a redox range of 18 oxygen fugacity log units, the incorporation of nitrogen in silicate melts equilibrated with the [C-N-O] vapor systems follows two different behaviors. For log fO<sub>2</sub> values between -0.7 and -10.7 (the latter corresponding to IW-1.3), nitrogen dissolves as a N<sub>2</sub> molecule into cavities of the silicate network (physical solubility). Nitrogen presents a constant solubility (Henry's) coefficient of  $2.21 \pm 0.53 \times 10^{-9} \text{ mol.g}^{-1}.\text{atm}^{-1}$  at 1425 °C, identical within uncertainties to the solubility of argon. Further decrease in the oxygen fugacity (log fO<sub>2</sub> between -10.7 and -18 corresponding to the range from IW-1.3 to IW-8.3) results in a drastic increase of the solubility of nitrogen by up to 5 orders of magnitude as nitrogen becomes chemically bounded with atoms of the silicate melt network (chemical solubility). The present results strongly suggest that under reducing conditions nitrogen dissolves in silicate melts as N<sup>3-</sup> species rather than as CN<sup>-</sup> cyanide radicals.

**Melt composition:** We also show that the effect of melt composition on nitrogen solubility depends on oxygen fugacity. Between air and IW-1, we found that nitrogen solubility is low and increases with the bulk polymerization of the melt, as rare gases do, in agree-

ment with a dissolution mechanism controlled by the steric effect of the N<sub>2</sub> molecule, filling holes of interstitial location of the silicate melt network. This contrast with results obtained in more reducing conditions (<IW-1), in which high N solubility is anticorrelated with the bulk polymerization of the melt due to the substitution of non-bridging oxygen for nitrogen in the melt silicate network, very likely by forming Si(O<sub>3</sub>N)<sup>5-</sup> structural groups where nitrogen is three-fold coordinated to silicon.

**Gas speciation:** If equilibration under H<sub>2</sub>-bearing gaseous environments don't alter the physical solubility of nitrogen between air and IW-1, we found that N solubility drops by ~33% by comparison with equilibration in H<sub>2</sub>-free vapors, due to the more complex speciation of nitrogen in these conditions, i.e., (NH<sub>2</sub><sup>-</sup>), (NH<sup>-</sup>) and (N<sup>3-</sup>) species.

All these results have important implications for the mechanisms of nitrogen dissolution in basaltic melts in both terrestrial and extra-terrestrial environments and complement our knowledge on nitrogen outgassing.

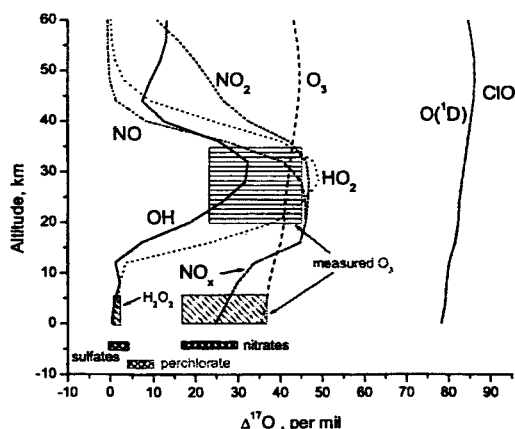
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**Oxygen Isotope Anomalies in the Atmospheres of Earth and Mars.** J. R. Lyons, Institute of Geophysics and Planetary Physics, UCLA, Los Angeles, CA 90095-1567; jrl@ess.ucla.edu.

The discovery of large enrichments of  $^{18}\text{O}$  in stratospheric ozone [1], and the demonstration of mass-independent fractionation (MIF) of oxygen isotopes ( $^{16}\text{O}$ ,  $^{17}\text{O}$ ,  $^{18}\text{O}$ ) in both laboratory-produced ozone [2] and atmospheric ozone [3] have opened up a new field of isotope atmospheric chemistry. Observations of MIF have been made in a wide variety of oxygen-containing atmospheric species [4], in effect, making MIF a tracer of ozone chemistry.

The signature of MIF has also been observed in sulfate [5] and nitrate aerosols [6], and is preserved after aerosol deposition in dry environments such as the Antarctic dry valleys and the Atacama desert. Anomalies in  $^{17}\text{O}$  allow us to trace atmospheric ozone chemistry into the surficial lithosphere.

Determination of isotopomer-specific rate coefficients for the ozone formation reaction proved that the MIF occurs during the formation step [7]. In addition, having isotopomer-specific rate coefficients for ozone formation makes it possible to quantitatively model the photochemistry and distribution of isotopologues of atmospheric species [8]. The figure below shows model results for  $\Delta^{17}\text{O}$  of several atmospheric species versus altitude. Also on the figure are the ranges of measured values for several aerosol and surface deposited sulfates [5] and nitrates [6], and perchlorate surface deposits [9].



The oxygen isotope anomalies ( $\Delta^{17}\text{O}$ ) of the nitrates are easily understood as resulting from isotope exchange between  $\text{NO}_2$  and  $\text{O}_3$ , followed by formation of nitric acid [6,8]. Sulfates acquire their anomalies from oxidation of  $\text{SO}_2$  by either  $\text{O}_3$  or  $\text{H}_2\text{O}_2$  in the

aqueous phase [10]. Perchlorate formation via heterogeneous reaction of  $\text{ClO}$  on sulfuric acid aerosols has been proposed for the stratosphere [11].

The preservation of oxygen isotope anomalies in particularly dry regions of the terrestrial surficial lithosphere bodes well for preservation of such anomalies on the surface of Mars. In fact, surface deposits on Mars are likely to be an important reservoir of  $\Delta^{17}\text{O}$  in the Martian atmosphere-hydrosphere-lithosphere system. Measurements of  $\Delta^{17}\text{O}$  of water [12], carbonates [13], and sulfates [14] in several SNC meteorites have shown anomalies of +0.3 to +1.0 per mil relative to SNC silicate.

It has been suggested [13,14] that mass-independent fractionation in the Martian atmosphere is responsible for the positive  $\Delta^{17}\text{O}$  measured in SNC secondary mineral phases. Possible MIF-producing reactions include 1) ozone formation followed by transfer to  $\text{CO}_2$  via  $\text{O}(^1\text{D})$ , 2) MIF during  $\text{CO}_2$  photolysis, and 3) MIF during the reaction  $\text{CO} + \text{OH} \rightarrow \text{CO}_2 + \text{H}$ . In addition to chemical MIF, oxygen isotope anomalies are predicted due to loss of O and H from the planet over time [15].

Based on terrestrial photochemical modeling of oxygen isotope anomalies [8] I will present initial results of a photochemical model for the Mars atmosphere. The immediate goal is to assess the possibility that chemical MIF is responsible for the observed in SNC meteorites, but the study also represents a potentially significant intercomparison between terrestrial and Mars oxygen isotope systematics.

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**THE EFFECT OF OXYGEN FUGACITY ON INTERDIFFUSION OF IRON AND MAGNESIUM IN MAGNESIOWÜSTITE.** S. J. Mackwell<sup>1</sup>, and M. Bystricky<sup>2</sup>. <sup>1</sup>Lunar and Planetary Institute, 3600 Bay Area Boulevard, Houston, TX 77058, <sup>2</sup>Geologisches Institut, ETH-Zentrum, Zürich, Switzerland.

**Abstract:** Magnesioiwüstite is the second most abundant mineral in the lower mantle of Earth and presumably Venus. As such its chemical, physical and mechanical properties will exert a significant influence on this region of the planets' interiors. Like most iron-bearing minerals, magnesioiwüstite possesses considerable non-stoichiometry, due to the presence of octahedral cation (metal) vacancies that charge compensate for ferric iron, which occupies either nominally 2+ octahedral cation sites, or tetrahedrally coordinated interstitial sites [1-2]. Past research has demonstrated that the degree of non-stoichiometry increases with increasing iron content and oxygen fugacity, and decreases with increasing temperature and pressure [2-5]. This non-stoichiometry exerts a tangible effect on a range of chemical and physical properties, ranging from diffusion through elastic behavior, electrical conductivity and deformation [6-10]. It also provides a natural site for occupancy by water-derived species, which in turn further affect crystal properties [11].

We have performed experiments to measure interdiffusion between iron and magnesium in magnesioiwüstite  $\text{Mg}_x\text{Fe}_{1-x}\text{O}$  over a range of temperature (1320 – 1400°C), oxygen fugacity ( $10^{-1}$  to  $10^{-4.3}$  Pa), and iron content ( $0.0 < x < 0.27$ ) at room pressure [12]. The oxygen fugacity was controlled using mixed gases of  $\text{CO}/\text{CO}_2$  or  $\text{H}_2/\text{CO}_2$ , so that we could also test for any major effects of water on the interdiffusion coefficient (even with mixed  $\text{H}_2/\text{CO}_2$ , the water fugacity at room pressure is very modest). The experiments were performed using a single crystal of  $\text{MgO}$  lightly loaded against a single crystal of  $\text{Mg}_x\text{Fe}_{1-x}\text{O}$  with  $0.06 < x < 0.27$ . After the experiments, the sample was cut in half and the compositional variation in Mg and Fe was measured using an electron microprobe across a cross section of the sample. Details of the measurement technique can be found in Mackwell et al. [12].

The diffusion profiles measured in this way were analysed using the Boltzmann-Matano analysis to yield values of the interdiffusion coefficient as a function of composition at each temperature and oxygen fugacity condition tested. No effect of water fugacity, over the narrow range of conditions tested, was detected. The interdiffusion coefficient was found to vary with an oxygen fugacity exponent of 0.19 and an activation energy for diffusion of 209 kJ/mol. The dependence of interdiffusion on iron concentration included both power law (with an exponent of 0.73) and exponential terms (96 kJ/mol), consistent with previous studies of interdiffusion in iron-bearing systems [13]. This result

is consistent with interdiffusion mediated by metal vacancies, and is consistent with previous studies of vacancy diffusion in magnesium oxide lightly doped with iron [8].

When used in concert with similar experiments performed at high pressure, these results support the conclusions of Holzapfel et al. [14] who suggested an activation volume for interdiffusion of around  $3.3 \times 10^{-6} \text{ m}^3/\text{mol}$ . Although not determined within the range of water fugacities available in these experiments, it is expected that the increase in metal vacancy concentrations resulting from incorporation of modest quantities of water-related species at high-pressure [11] will result in a significant increase in the rate of interdiffusion, as well as other physical properties, such as creep and electrical conductivity.

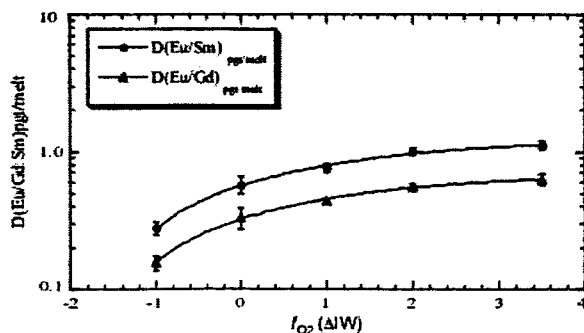
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**THE CALIBRATION OF THE PYROXENE EU-OXYBAROMETER FOR THE MARTIAN METEORITES.** M. C. McCanta<sup>1,2</sup> and M. J. Rutherford<sup>1</sup>, <sup>1</sup>Brown University, Dept. of Geological Sciences, Box 1846, Providence, RI, 02912, molly\_mccanta@brown.edu, <sup>2</sup>Lunar and Planetary Institute, 3600 Bay Area Blvd., Houston, TX 77058.

**Introduction:** Oxygen fugacity ( $f_{O_2}$ ) is the physical parameter used to describe oxidation state.  $f_{O_2}$  influences both the crystallization sequences of magmas and the composition of the resulting minerals [e.g., 1,2]. Therefore, by quantifying the crystallization  $f_{O_2}$  of a magma, insights can be gained into conditions of the magma storage region (i.e., a planetary interior). One of the first phases on the basaltic shergottite liquidus is the low-Ca pyroxene pigeonite. By measuring the  $f_{O_2}$  recorded in the pigeonite cores, the earliest crystallization history of the Martian magmas can be determined. In order to quantify the  $f_{O_2}$  recorded in the pigeonites, a new technique was required. It had been noted that the  $Eu^{2+}/Eu^{3+}$  ratio in pyroxenes was a function of  $f_{O_2}$  [3,4], but this potential oxybarometer had never been calibrated for pigeonite. This study describes the calibration of the pigeonite Eu-oxybarometer.

**Experimental Methods:** Dry crystallization experiments were performed on a synthetic shergottite melt in equilibrium with liquidus pyroxenes [5, 6]. The melt was doped with ~1 wt.% each of  $Eu_2O_3$ ,  $Gd_2O_3$ , and  $Sm_2O_3$  following the method of [4]. Experimental  $f_{O_2}$  values ranged from QFM (IW+3.5) to IW-2. Samples were suspended on Re-loops in 1-atm, CO-CO<sub>2</sub> gas mixing furnaces at JSC. All experimental glasses and pyroxenes were probed on the electron and ion microprobes (SIMS). Geochemical data for the meteorites was taken from [7]. Pyroxene core REE contents were used in  $f_{O_2}$  calculations, reflecting the earliest magmatic history.

**Results:** The results of the calibration experiments are presented in Figure 1. The systematic variation of the D-values with  $f_{O_2}$  indicates the utility of the pigeonite Eu-oxybarometer. The SNC meteorites exhibit a 2-3 order magnitude range of crystallization  $f_{O_2}$  values as recorded in the pigeonites (Figure 2).

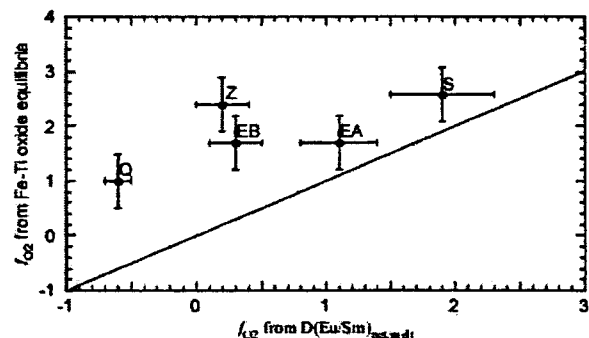


**Figure 1.** Calibration of  $D(Eu/Gd)_{\text{pigeonite/melt}}$  and  $D(Eu/Sm)_{\text{pigeonite/melt}}$  versus  $f_{O_2}$  (in log units relative to the IW buffer).

**Issues with Gd.** Calculations of  $f_{O_2}$  made using Gd ion probe measurements proved problematic. Due to its low

concentrations and peak interferences with other REEs, Gd in the natural samples cannot be directly measured by SIMS. The Gd content is extrapolated in reference to the surrounding REE values [8]. This introduces large errors into the Gd values of the SNC pyroxenes which in turn propagate through the Eu-oxybarometer calculations. Sm content can be directly measured by SIMS, therefore only the oxybarometer based on Eu and Sm values is used for the following SNC  $f_{O_2}$  measurements.

**Implications:** Several theories have been proposed to explain the range of SNC  $f_{O_2}$  values, several of which rely on a late-stage assimilation event [e.g., 9,10]. A comparison between  $f_{O_2}$  values recorded in different SNC phenocryst phases may clarify this issue. As mentioned previously, pigeonite is one of the earliest crystallizing phases on the SNC liquidus. In contrast, Fe-Ti oxides are late-stage phases [e.g., 11]. Remarkably, the two most oxidized meteorites studied, Shergotty and EETA79001A, record similar  $f_{O_2}$  values in both the early and late crystallizing phases (Figure 2). This suggests that the  $f_{O_2}$  was internally buffered throughout the crystallization history of the meteorite, implying a heterogeneous magma source region. The range of observed  $f_{O_2}$  values is therefore not well explained by assimilation, but rather, could be achieved through crystallization of a Martian magma ocean [i.e., 12].



**Figure 2.** Comparison of  $f_{O_2}$  calculated using the dry pigeonite Eu-oxybarometer versus Fe-Ti oxide equilibria (Herd *et al.*, 2001). S: Shergotty, EA: EETA79001 lithology A, EB: EETA79001 lithology B, Z: Zagami, Q: QUE94201.

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**THE EUROPIUM OXYBAROMETER: POWER AND PITFALLS.** G. McKay, Mail Code SR, NASA Johnson Space Center, Houston, TX 77058, USA (Gordon.mckay@jsc.nasa.gov).

**Introduction:** One of the most important characteristics of a planet is the oxidation state of its mantle, as reflected in primitive basalts. Petrologists have devised several methods to estimate the oxygen fugacity under which basalts crystallized. One method that has been the subject of recent interest involves the depth of the Eu anomaly in first-crystallizing minerals.

Philpotts [1] was the first to suggest that the depth of Eu anomalies could be used to estimate redox conditions. Drake [2] was the first to calibrate this oxybarometer through experimental measurement of plagioclase/melt partition coefficients, and Weill *et al.* [3] formulated a theoretical model for the expected variation of  $D(\text{Eu}, \text{S/L})$  with  $f\text{O}_2$ .

**Ratios are better:** McKay *et al.* [4] noted that the ratio of partition coefficients,  $D(\text{Eu}/\text{Gd}, \text{Px/L})$ , is less susceptible to variations in phase composition (e.g., Al content of pyroxene) than are individual partition coefficients. Consequently, he recast the formulation of [3] in terms of partition coefficient ratios. He further noted that if two minerals are present that were both in equilibrium with the same liquid, the formulation could be further recast as the ratio of partition coefficients between the two minerals, thus eliminating the liquid. This is a major advantage because the REE concentrations in the parent melt of a sample are rarely known with certainty.

**Experimental Calibration:** In the formulation of [4], the ratio of Eu and Gd partition coefficients for a mineral varies along S-shaped curves that approach  $D(\text{Eu}^{+2})/D(\text{Gd})$  at low  $f\text{O}_2$  and  $D(\text{Eu}^{+3})/D(\text{Gd})$  at high  $f\text{O}_2$ , as shown in Fig. 1. The symbols in Fig. 1 are experimentally determined plagioclase/melt and pyroxene/melt partition coefficient ratios ( $D(\text{Eu}/\text{Gd})$ ) measured in a system with the bulk composition of angrite

LEW 86010 [4]. The curves in Fig. 1 are the result of least-squares fits of model parameters to the observed data.

**Application to Angrites:** McKay *et al.* [4] combined the curves in Fig. 1 with analyses of plagioclase and fassaite [5] to solve for the  $f\text{O}_2$  of LEW. They concluded that LEW crystallized at  $\log f\text{O}_2$  of  $\sim \text{IW}+1$ , more than two log units higher than eucrites [6].

**Application to Martian Basaltic Meteorites:** Using the pyroxene calibrations of [4], Wadhwa [7] applied the Eu oxybarometer to shergottites. She assumed that the REE content of the bulk rock approximated the melt, and that the pyroxene cores that she analyzed by SIMS were in equilibrium with that melt. She concluded that the  $f\text{O}_2$  under which shergottites crystallized ranged from  $\sim \text{IW}-1$  to  $\sim \text{IW}+2$ , suggesting complex petrogenetic processes.

**Strengths of the Eu Oxybarometer:** (1) The Eu oxybarometer has an important advantage over oxide oxybarometry [e.g., 4]: Oxides can be highly susceptible to subsolidus reequilibration, whereas the REE contents of the cores of liquidus silicate minerals are much less likely to change after crystallization. (2) Ratios of partition coefficients are less susceptible to compositional dependence than individual partition coefficients (see below). (3) As noted above, use of two coexisting silicates can eliminate assumptions about melt composition.

**Weaknesses:** (1) REE analyses of the cores of liquidus minerals are required. Usually such analyses are best obtained by SIMS, a technique that is not widely available. (2) Partition coefficients are dependent on phase composition, particularly pyroxene Ca content and, to a lesser extent, Al content. Use of partition coefficient ratios reduces the compositional dependence [e.g., 4], but may not eliminate it entirely. There is a very large compositional difference between the fassaitic pyroxenes in angrites and the sub-calcic augites and pigeonites in shergottites. Nevertheless, recent studies [9,10] suggest that the angrite calibration [4] is generally applicable to shergottites. However but a focused study of compositional influence could strongly reinforce this conclusion.

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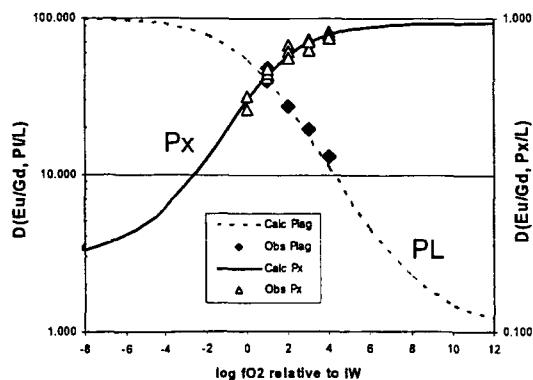


Figure 1. Calibration of  $D(\text{Eu}/\text{Gd})$  for angritic plagioclase and pyroxene from [4].

**OXYGEN FUGACITY OF THE MARTIAN MANTLE FROM PIGEONITE/MELT PARTITIONING OF SAMARIUM, EUROPIUM AND GADOLINIUM** D. S. Musselwhite<sup>1</sup>, J. H. Jones<sup>2</sup>, and C. Shearer<sup>3</sup> <sup>1</sup>Lunar and Planetary Institute (3600 Bay Area Blvd., Houston, TX 77058, musselwhite@lpi.usra.edu), <sup>2</sup>Astromaterials Research Office (NASA/JSC, Mail Code SR, Houston, TX 77058, john.h.jones1@jsc.nasa.gov) <sup>3</sup>Institute for Meteoritics (Univ of New Mexico, Albuquerque, NM 87131, cshearer@unm.edu)

**Introduction:** This study is part of an ongoing effort [1,2] to calibrate the pyroxene/melt Eu oxybarometer [3] for conditions relevant to the martian meteorites. There is fairly good agreement between  $fO_2$  determinations using equilibria between Fe-Ti oxides [4,5] and the estimates from Eu anomalies in shergottite augites [6] in terms of which meteorites are more or less oxidized. However, there is as much as two log-units offset in  $fO_2$  values between the results of [4,5] and [6]. The Eu calibration used by [6] was for angrite composition pyroxenes [7] which are rather extreme. However, application of a calibration for martian composition augites [1] does not significantly reduce the discrepancy between the two methods. One possible reason for this discrepancy is that augites are non-liquidus. The use of pigeonite rather than augite as the oxy-barometer phase is considered. We have conducted experiments on martian composition pigeonite/melt REE partitioning as a function of  $fO_2$ .

**Methods:** Pigeonite/melt partitioning experiments for Sm, Eu and Gd were run in a gas-mixing DelTec furnace at  $fO_2$ s ranging from one log unit below to four log units above the iron-wüstite buffer. The starting composition was doped with 1% each of Sm, Eu and Gd. Sample preparation and experimental procedures are the same as in [1]. Run products were analyzed for all elements with the SX100 EMP at NASA/JSC. In addition, trace element analyses of the pyroxene and glass were conducted using the Cameca ims 4f ion microprobe at UNM.

**Results:** Experimental pigeonite compositions lie at the more magnesian and lowest calcium end-member of the natural pigeonite cores [8,9]. The ratio of  $D_{Eu}$  to  $D_{(Sm,Gd)}$  (pig./melt) as a function of  $fO_2$  from these experiments is shown in fig 1.

**Discussion:** Applying fig. 1 data to D ratios from measured REE concentrations in shergottite pigeonite cores [10] and whole rocks [11] gives the  $fO_2$  for each meteorite at the time of initial pigeonite crystallization. These values are plotted in Fig 2 against the  $fO_2$ s derived from Fe-Ti oxides.

There is, to first order, good agreement between the  $fO_2$ s determined from the Eu-anomaly method with the calibration presented here and those using the Fe-Ti oxide method. There is a subtle tendency for the values to be shifted from the 1:1 correspondence line depending on  $fO_2$ . The similarity of results between the two methods leads us to believe that we are on the right track in the use of

pigeonite for the  $fO_2$  determination and that the calibration is applicable.

Further work on this subject is concentrating on identification of the truly first formed pigeonite and augite cores in basaltic shergottites and analysis with both SIMS and LAM-ICPMS methods in an effort to produce the best rare earth ratios and to reduce the associated error. Further experiments are also under way to cover the range of martian pigeonites.

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Fig 1:

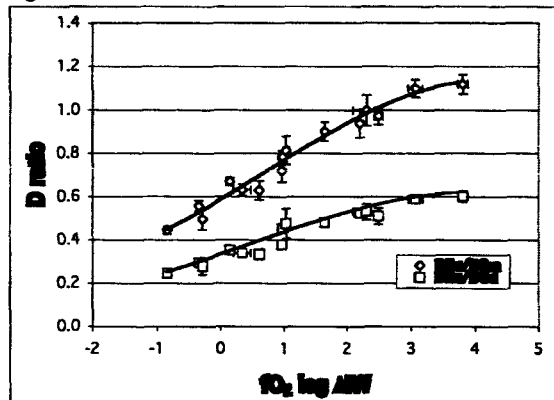
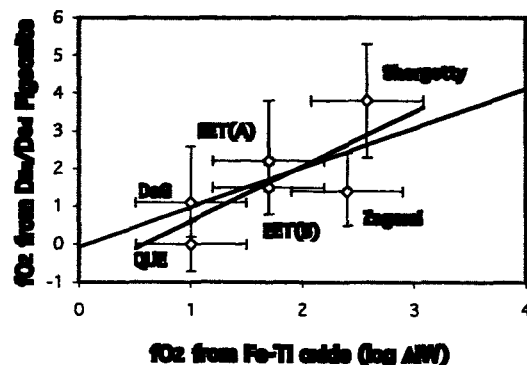


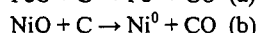
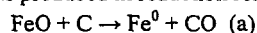
Fig 2:



**OXIDATION-REDUCTION PROCESSES ON THE MOON: EXPERIMENTAL VERIFICATION OF GRAPHITE OXIDATION IN THE APOLLO 17 ORANGE GLASSES.** M. G. Nicholis<sup>1</sup> and M. J. Rutherford<sup>1</sup>,  
<sup>1</sup>Department of Geological Sciences, Brown University Providence, RI: [Mike\\_Nicholis@Brown.edu](mailto:Mike_Nicholis@Brown.edu), and [Malcolm\\_Rutherford@Brown.edu](mailto:Malcolm_Rutherford@Brown.edu).

**Introduction:** It is widely believed that a volatile-driven fire-fountain eruption produced the Apollo 17 orange glass deposit [1]. The picritic composition of these glasses indicate that they maybe the primitive analogs of mare basalts, and hence may be a window into the evolution of the lunar interior. However, to understand the petrogenesis of the picritic glasses it is essential to verify and constrain the volatile generating mechanism driving the eruption as well as the volatile budget during magma ascent in the conduit.

Fogel and Rutherford [2] have shown that the oxidation of graphite suspended in the melt and/or present in the source region, as proposed by [3], was alone capable of fueling a fire-fountain event. Further analysis of metal blebs found in the orange glasses by [4] indicated that CO, the main component of the gas phase, was produced in reduction reactions such as:



when the ascending magma intersected the graphite oxidation surface (Figure 1). Their calculation of the intrinsic  $f\text{O}_2$  of the orange glass (IW - 1.3) suggested that oxidation occurred at a depth of 4 km (~200 bars). [5] analyses of melt inclusions in olivine phenocrysts found in the glass beads and analyses of the beads themselves revealed a dichotomy in their S and Cl concentrations. They found a 400 ppm difference in S content between the glasses and melt inclusions. This dichotomy along with surface-coatings on the glass beads enriched in volatile elements such as C, S, Na, K, Cl, F, P, and Zn [6] suggest that the glass beads were in contact with a gas phase more complex than a simple CO-CO<sub>2</sub> gas mixture. [4] suggested that the release of these volatile elements into the gas phase resulted in an oxidation of Fe<sup>0</sup> in the metal blebs. This oxidation is represented by a concentration profile resulting in Fe-depleted and Ni-enriched rims in metal blebs in the glasses.

The assessment on the depth of graphite oxidation, volatile content and composition of the gas phase, and the oxidation of the metal blebs have all come from analytical and theoretical interpretations. In this investigation, we provide a comprehensive experimental evaluation on the influence of graphite oxidation on the Apollo 17 orange glass composition, and the gas phase which was generated during the eruption.

**Experimental Methods:** Compressed sintered pellets of synthetic picritic orange glass composition were placed in Pt capsules lined with graphite powder. The C powder served multiple functions which included inhibiting melt contact with the Pt capsule walls, fixed the  $f\text{O}_2$  to lunar conditions, and reacted with the melt to generate the CO-CO<sub>2</sub> gas phase. Isothermal (1320°C) experiments were conducted in a Harwood internally heated pressure vessel for a pressure range of 200-

700 bars and a time duration of 3-4 hours. The first set of experiments attempt to locate the critical pressure of the graphite oxidation surface for the synthetic lunar orange glass composition. We then intend to explore the sensitivity of the oxidation surface with similar experiments using S-bearing, Cl-bearing, and both S- and Cl-bearing synthetic glass compositions. Which will allow one to investigate the partitioning of S and Cl between the melt and gas phases.

**Results:** Our initial experiments indicate that the critical pressure of 200 bars, as proposed by [4], is the approximate pressure where the graphite oxidation surface is crossed and graphite lining the capsule reacts with the melt to produce a CO-CO<sub>2</sub> gas phase. As a result of graphite oxidation, FeO in the melt is reduced to form a metal phase. Further graphite oxidation results in an increase in metal production and a decrease in melt FeO content.

**Implications:** Results from these experiments verify the pressure sensitivity of the graphite oxidation surface for an  $f\text{O}_2$  within the range of the lunar interior. Experiments in progress will quantify the influence of S- and Cl-bearing glass compositions on the oxidation surface and their partitioning into the gas phase. These experiments will also help identify the subsequent oxidation process which produced the Ni-rich rims on metal blebs found in the orange glass.

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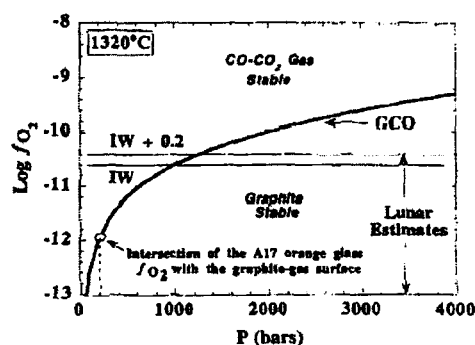


Figure 1. Plot of graphite-CO oxidation surface (GCO) as function of oxygen fugacity and pressure taken from [4].

**OXYGEN AND CORE FORMATION IN THE EARTH.** Hugh St.C. O'Neill, Research School of Earth Sciences, Australian National University, Canberra, ACT 0200, Australia

Core formation in the Earth is ultimately dependent on the net redox state of the material from which the Earth accreted (i.e., ratio of silicate plus oxide material to metal). This ratio is a direct reflection of the material's oxygen content. A planet formed of fully oxidized material (as in CI chondrites) could not form a metallic core. Oxygen is the third most abundant element in the solar system (after H and He) and the most abundant element in the Earth, comprising 44.3% by weight of the Earth's mantle [1]. The O content of the bulk Earth is thus ~30%, and in detail slightly higher depending on how much O comprises the light component in the Earth's core. The Earth's O/Mg ratio is ~2.0, which compares with ~5 in CI chondrites and 14.6 in the solar composition [2]; thus the Earth has only a small fraction of the O available in the solar composition, hence the metallic core.

The ratio of silicate to metal is set by the behaviour of O during condensation from the solar nebula, which behaviour is unique among the elements, in that significant quantities of O condense early (O associated with Al, Ca etc in refractory oxides) but much O is also a highly volatile and only condenses late as ices (H<sub>2</sub>O, CO<sub>2</sub>). In between, O condenses with decreasing nebular temperature first by oxidation of Fe metal to form Fe<sup>2+</sup>-containing silicates [3]; then, when nearly all Fe<sup>0</sup> is oxidized, further condensation occurs by oxidation of Fe<sup>2+</sup> to Fe<sup>3+</sup> (e.g., to form Fe<sub>3</sub>O<sub>4</sub>), of Ni<sup>0</sup> to Ni<sup>2+</sup> and sulfide to sulfate, and by formation of H<sub>2</sub>O-containing minerals (serpentine minerals and epsomite). The increase in O content with decreasing condensation temperature implies that the redox state of planet-forming materials should correlate with their volatile element inventories. Material with all Fe as Fe<sup>2+</sup> should be rich in moderately volatile elements and may contain H<sub>2</sub>O, but material with Fe metal should contain negligible H<sub>2</sub>O. The presence of both a large metallic core and significant amounts of H<sub>2</sub>O in the Earth is an anomaly whose resolution should reveal much about the formation of the terrestrial planets.

Similarly, it has long been known that the pattern of the abundances of the siderophile elements in the Earth's mantle is highly anomalous compared to that expected for low-pressure partitioning between silicate and metal. Historically, two classes of explanation have been assumed as working hypotheses to explain this anomaly: 1) the Earth formed heterogeneously, from a mixture of materials with different redox states; 2) accretion was

heterogeneous, and the pattern reflects partitioning at very high pressures and temperatures such as are only achievable in a planet of Earth-like size. Scenarios for heterogeneous accretion can be constructed that satisfy most of the observational constraints, but are considered intellectually less compelling than homogeneous accretion models because of their necessarily ad-hoc nature. Conversely, an undiluted homogeneous accretion model that seeks to find a single condition of pressure, temperature and light component in the core that can explain every nuance of the mantle siderophile element pattern appears improbable and unrealistic, such that some aspect of heterogeneous accretion will always need to be invoked – a “late veneer” to explain platinum group element abundances, for example. This also appears likely on dynamical grounds. Our current state of knowledge is such that the question should now centre on the extent to which the signature of metal/silicate chemical equilibration in the mantle is due to the high pressures obtained in the Earth during accretion, or to low-pressure conditions in the small planetesimal-sized bodies from which the Earth formed. This question also bears on the timing of core formation, and the nature of the light component in the core. This latter, whose identity is a long-standing mystery, was postulated because of an apparent deficit between the density of the Earth's core as inferred from geophysical observations, and the calculated density of Fe-Ni metal at core P-T conditions. While O was considered a possibility if metal/silicate formation occurred at high pressures, new measurements of the solubility of O in Fe-metal shows that it decreases with increasing pressure under appropriate terrestrial parageneses, making it an unlikely candidate. Indeed, on geochemical grounds there seems to be no element sufficient to explain the traditional density difference, leading to a recent reappraisal of the magnitude of this deficit [4]. It is also possible that under a plausible geodynamic regime at the core-mantle boundary, there might be significant exchange of O between core and mantle, thus a change in O content of the core with time [5].

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**GEOLOGIC RECORD OF THE ATMOSPHERIC SULFUR CHEMISTRY BEFORE THE OXYGENATION OF THE EARLY EARTH'S ATMOSPHERE.** S. Ono,<sup>1</sup> B. Wing<sup>2</sup>, J. Eigenbrode<sup>1</sup>, D. Rumble<sup>1</sup>, and J. Farquhar<sup>2</sup>, <sup>1</sup>Geophysical Laboratory, Carnegie Institution of Washington, 5251 Broad Branch Rd., NW, Washington DC 20015 ([s.ono@gl.ciw.edu](mailto:s.ono@gl.ciw.edu)), <sup>2</sup>Department of Geology and ESSIC, University of Maryland College Park, MD 20742

Mass-independent fractionation (MIF) signatures recorded sulfide and sulfate minerals in rocks older than 2.45 Ga suggest a fundamental change in the biogeochemical sulfur cycle took place between 2.45 and 2.0 Ga, most likely reflecting an oxygenation of the Earth's early atmosphere [1-6]. We will present multi-sulfur isotope records of a late Archean sedimentary sequence in the Hamersley Basin, Australia (~2.7 to 2.4 Ga). These data, placed in a context of modeled isotope systematics and depositional environments, provide new insights into sulfur biogeochemical cycle prior to the oxygenation of the Earth's atmosphere.

Multi-sulfur (<sup>32</sup>S, <sup>33</sup>S, <sup>34</sup>S, and <sup>36</sup>S) isotope records in the Hamersley Basin, Australia are characterized by the largest variation in  $\delta^{33}\text{S}$  ( $\delta^{33}\text{S} = \sim \delta^{33}\text{S} - 0.5 \times \delta^{34}\text{S}$ ; +8.2 to -2.5 ‰) [4]. These non-zero  $\delta^{33}\text{S}$  values suggest an anoxic (or reducing) atmosphere with  $p\text{O}_2$  of less than  $10^{-6}$  atmosphere during 2.4 to 2.7 Ga [2,4]. In contrast, steranes, lipid biomarkers for eukaryotes, have been reported in the same drill cores studied, suggesting the presence of some molecular oxygen in the environment [7,8]. These two apparently contradicting geochemical evidences can be reconciled by the idea of "oxygen oasis" in the late Archean. Such that, molecular oxygen was limited within the productive area of surface ocean (and within biomats) and atmosphere was essentially devoid of oxygen [9].

A correlation between  $\delta^{33}\text{S}$  and  $\delta^{36}\text{S}$  ( $\delta^{36}\text{S} = \sim \delta^{36}\text{S} - 1.9 \times \delta^{34}\text{S}$ ) was found over a much wider range of  $\delta^{33}\text{S}$  than those reported in [1] by a newly developed *irm*-GCMS system at Geophysical Laboratory and a conventional dual inlet system at the University of Maryland. This well defined correlation excludes the nuclear synthesis and nuclear-electron spin-coupling for the origin of mass-independent sulfur isotope fractionation, supporting atmospheric origin of Archean sulfur MIF. Laboratory experiments undertaken with  $\text{SO}_2$  and UV radiation at 193 nm and < 220 nm are currently the only known process to produce similar relationships. Notably, our samples are from four drill cores from 2.45 Ga to 2.7 Ga in age. The constant relationship between  $\delta^{33}\text{S}$  and  $\delta^{36}\text{S}$  may suggest that the major reaction pathway responsible for sulfur MIF

signatures in Archean atmosphere had not changed over ~ 250 million years.

Multi-sulfur isotope records show lithologic dependence. Hemipelagic carbonaceous shales are characterized by large positive  $\delta^{33}\text{S}$  values. Sulfide sulfur form one core of the Mt. McRae shale (~2.5 Ga) and two cores of the Jeerinah formation (~2.7 Ga) drilled >200 km apart show similar correlation between  $\delta^{33}\text{S}$  and  $\delta^{34}\text{S}$  [4]. However, values of  $\delta^{33}\text{S}$  and  $\delta^{34}\text{S}$  do not correlate for sulfides from platform carbonates. This suggests superposition of bacterial mass-dependent fractionation signatures on the atmospheric MIF signatures, specifically suggesting the importance of sulfate reducing bacteria in the carbonate platform environment in the late Archean. Thus, multi-sulfur isotope system can be used to trace not only atmospheric processes but also the microbial sulfur cycle in the early ocean [4].

Detailed documentation of multiple sulfur isotope systematics and integration to the lithologic records helps us to deconvolve mass-independent atmospheric fractionation and biogenic mass-dependent fractionation, allowing us to better understand the early sulfur cycle and its linkage to the evolution of the early Earth's atmosphere.

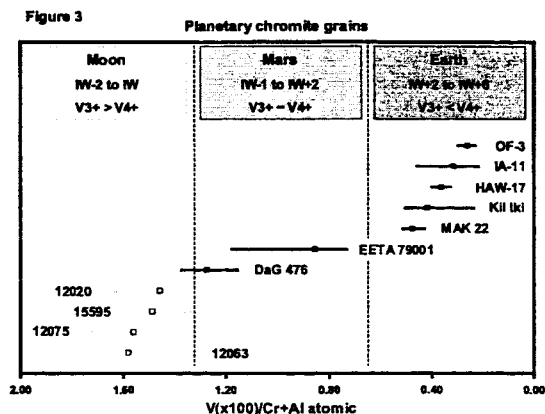
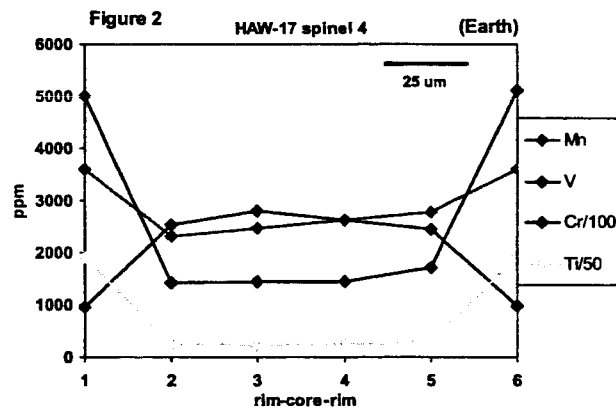
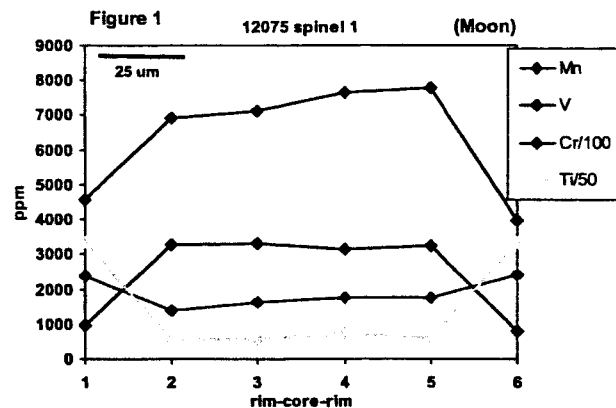
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**COMPARATIVE PLANETARY MINERALOGY: V/(Cr + Al) SYSTEMATICS IN CHROMITES AS AN INDICATOR OF RELATIVE OXYGEN FUGACITY.** J.J. Papike (jpapike@unm.edu), J.M. Karner, and C.K. Shearer, Institute of Meteoritics, Department of Earth and Planetary Sciences, University of New Mexico, Albuquerque, NM 87131-1126

As our contribution to the new "Oxygen in the Solar System" initiative of the Lunar and Planetary Institute and the NASA Cosmochemistry Program, we have been developing oxygen barometers based largely on behavior of V which can occur in four valence states V<sup>2+</sup>, V<sup>3+</sup>, V<sup>4+</sup>, and V<sup>5+</sup>, and record at least 8 orders of magnitude of  $fO_2$ . Our first efforts in measuring these valence proportions were by XANES techniques in basaltic glasses from Earth, Moon, and Mars [1,2]. We now address the behavior of V valence states in chromite in basalts from Earth, Moon, and Mars. We have been looking for a "V in chromite oxybarometer" that works with data collected by the electron microprobe and thus is readily accessible to a large segment of the planetary materials community. This abstract describes very early results that will be refined over the next two years. Our first insights into this new technique resulted from running probe scans on spinel grains for Cr, Al, Ti, Fe, Mg, Mn, and V from core to rim on grains which show zoning from chromite to ulvöspinel (Figures 1,2). The zoning profiles showed the normal trends of core to rim decreases of Cr, Al, Mg, and increases of Fe, Ti, and Mn. However, much to our delight, the V behavior was very different for Moon and Earth with Mars in between. In terrestrial basalts V<sup>4+</sup> > V<sup>3+</sup>, in lunar basalts V<sup>3+</sup> > V<sup>4+</sup>, and in martian basalts V<sup>3+</sup> and V<sup>4+</sup> are both significant [1,2]. The trends (core to rim) for the Moon show a strong positive correlation of V and Cr and negative correlation of V and Ti. For the Earth the trends were just the opposite with strong negative correlation for V and Cr and a strong positive correlation of V and Ti. Chromites in martian basalts showed trends somewhere in between with DaG 476 showing lunar type trends and EETA 79001 (lithology A) showing terrestrial type trends. According to [3,4] EETA (lithology A) crystallized at a higher  $fO_2$  than DaG 476. We found that a convenient way to display these data for chromites is a plot showing the relative V/(Cr + Al) ratios (Figure 3). These ratios nicely differentiate the oxygen fugacity ranges for Moon, Mars, and Earth. Our future work will attempt to make these results more quantitative. Canil [5] has already done such experiments for several basalt and chromite compositions and showed that  $D_V$  spinel/melt increases dramatically from ~2 at high  $fO_2$  (IW+5) to ~32 at low  $fO_2$  (IW-2).

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**HOW WELL DO SULFUR ISOTOPES CONSTRAIN OXYGEN ABUNDANCE IN THE ANCIENT ATMOSPHERES?** A. A. Pavlov, M. J. Mills, and O. B. Toon, Laboratory for Atmospheric and Space Physics, University of Colorado at Boulder, 392 UCB, Boulder, CO 80309-0392; pavlov@lasp.colorado.edu.

Oxygen abundance in the ancient terrestrial atmosphere is a fundamental and poorly resolved problem. Without "samples" of the ancient atmospheres scientists had to rely on the indirect constraints from the incomplete and heavily altered geological record. Fortunately, discovery of mass-independent fractionation (MIF) in sulfur isotopes in the Archean sediments and lack of MIF in sulfur in the younger rocks [1] placed a strict upper constraint on the amount of oxidants and oxygen in the ancient Earth's atmosphere prior to 2.3 Gyr ago [2]. MIF in sulfur isotopes can be produced only in the atmosphere and subsequent isotopic fractionation in the sediments can only destroy MIF but not create it. Preservation of MIF in the Archean sediments requires sulfur deposition from the Archean atmosphere in the variety of oxidation states ( $\text{SO}_2$ ,  $\text{H}_2\text{S}$ ,  $\text{S}_8$ ,  $\text{H}_2\text{SO}_4$  etc.) so that sulfur-bearing species would not completely rehomogenize sulfur isotopes before incorporation into the ancient rocks. Pavlov & Kasting [2] showed that it would be only possible if the ancient  $\text{pO}_2$  level were less than  $10^{-5}$  PAL (present atmospheric level).

However recent measurements by [3] in the Antarctic ice core showed a small but non-zero MIF in sulfate correlated with the large volcanic eruptions, raising questions about the sulfur MIF sensitivity to oxygen levels.

We put sulfur isotopes into a 2-D photochemical/microphysical model and looked at how strong the initial atmospheric fractionation had to be in order to be preserved in the Antarctic ice-cores. We will discuss two possibilities to preserve small sulfur MIF in the present atmosphere: (1) preservation through polar sulfate mesopause aerosols (2) preservation through the alternative pathway of  $\text{SO}_2$  oxidation [3].

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**EXPERIMENTAL CONSTRAINTS ON THE OXYGEN ISOTOPE ( $^{18}\text{O}/^{16}\text{O}$ ) FRACTIONATION IN THE ICE/VAPOR AND ADSORBATE/VAPOR SYSTEMS OF  $\text{CO}_2$  AT CONDITIONS RELEVANT TO THE SURFACE OF MARS.** Thom Rahn<sup>1</sup> and John Eiler<sup>2</sup>, <sup>1</sup>Earth and Env. Sci. Div., EES-6 MS-D462, Los Alamos Nat. Lab., Los Alamos, NM 87545, trahn@lanl.gov; <sup>2</sup>Div. of Geological and Planetary Sciences, MC 100-23, California Institute of Technology, Pasadena, CA 91125, eiler@gps.caltech.edu..

**Introduction:** A large fraction of the volatile oxygen on Mars is sequestered in carbon dioxide ( $\text{CO}_2$ ) that is partitioned between the atmosphere, polar caps and adsorbed in the regolith [1]. The stable isotopic composition of this  $\text{CO}_2$  can help constrain the origin and evolution of the respective  $\text{CO}_2$  reservoirs but is interpretable only with knowledge of fractionations relevant to Martian surface conditions. We review here results of previous experimental investigations of isotopic fractionations of  $\text{CO}_2$  vapor relative to  $\text{CO}_2$  ice and  $\text{CO}_2$  vapor relative to  $\text{CO}_2$  adsorbed on various mineral substrates. These experiments indicate that variations in ice-cap size and the amount of  $\text{CO}_2$  stored in the regolith, over a range of time scales, could lead to variations in  $\delta^{18}\text{O}$  on the order of tens of per mil. In addition, carbon isotopic ( $^{13}\text{C}/^{12}\text{C}$ ) content is nearly invariant in the ice/vapor system and exhibits 'reverse' fractionation in the adsorbate/vapor system, i.e. the heavier  $^{13}\text{C}$  preferentially remains in the vapor phase. Investigations searching for isotopic evidence for the existence of past or present life on Mars must take these unique constraints into account when interpreting records of Martian O and C isotopes.

**Experimental Methods:** Experiments described used one of a selection of cold traps that were developed for the purpose of well controlled temperature and pressure regimes in the range of Martian surface conditions. Ice/vapor experiments followed protocols that either 1) quantitatively condensed  $\text{CO}_2$ , subsequently warmed the trap to the desired temperature, and collected and measured the isotopic content of the vapor fraction (sublimation protocol) 2) introduced  $\text{CO}_2$  vapor to a trap held at constant T for a variable period of time prior to sampling (condensation protocol) 3) exchange experiments as per the condensation protocol after which the head space was evacuated and  $\text{CO}_2$  vapor of a very different isotopic content was introduced to the already condensed ice fraction (exchange protocol) [2]. Adsorbate/vapor experiments essentially followed the same protocols but with one of three different mineral substrates (crushed basalt, kaolinite or fluorite) loosely packed in the cold trap. In addition,  $\text{CO}_2$  adsorbed on mineral substrates exhibited complex O isotope behavior that led to the design of a cold trap that could be 'baked' prior to introduction of  $\text{CO}_2$  [3].

**Results and Discussion:** Ice/vapor experiments show that O isotope fractionation (defined as  $\Delta_{\text{ice-vapor}} = 1000 \cdot \ln([^{18}\text{O}_{\text{ice}}/^{16}\text{O}_{\text{ice}}]/[^{18}\text{O}_{\text{vapor}}/^{16}\text{O}_{\text{vapor}}])$ ) varies approximately linearly between temperatures

of 150 and 130 K, from 4.2 to 7.5 ‰ respectively (see Fig. 1). Oxygen isotope fractionation in the adsor-

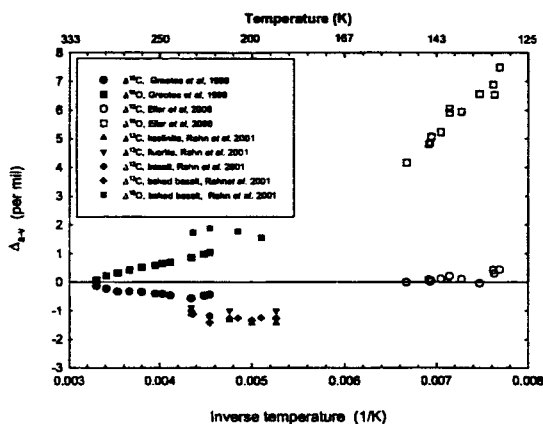


Figure 1: Plot of C and O fractionation in different systems as noted in the legend. Grootes et al. liquid/vapor [4], Eiler et al. ice/vapor [2], Rahn et al. adsorbate/vapor [3]. From Rahn et al. [3].

bate/vapor system exhibited complexity that we attribute to residual adsorbed  $\text{H}_2\text{O}$  on the mineral substrate. Comparison of experiments using vacuum-baked substrates to those on un-baked substrates suggests that exchange between one or both phases of  $\text{CO}_2$  and  $\text{H}_2\text{O}$  adsorbed on the sample surfaces influences the  $^{18}\text{O}/^{16}\text{O}$  fractionation between vapor and adsorbate and changes the  $^{18}\text{O}/^{16}\text{O}$  composition of the total  $\text{CO}_2$ . On vacuum-baked substrates, 'normal' fractionation (that is,  $^{18}\text{O}$  preferentially partitioned into the adsorbed  $\text{CO}_2$ ) was observed,  $\Delta_{\text{ads-vapor}} \sim 1.8$  ‰ (Fig. 1), with no measurable temperature dependence. No evidence was found for exchange of O isotopes between structural oxygen in mineral substrates and adsorbed  $\text{CO}_2$ . Depending on the fraction of  $\text{CO}_2$  condensed (as ice or adsorbed) and the degree of communication between condensed and vapor fractions, residual vapor may be enriched by as much as tens of per mil relative to the initial  $\text{CO}_2$  reservoir.

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**MICRO-XANES MEASUREMENTS ON EXPERIMENTAL SPINELS AND THE OXIDATION STATE OF VANADIUM IN SPINEL-MELT PAIRS.** K. Righter<sup>1</sup>, S.R. Sutton<sup>2,3</sup>, and M. Newville<sup>3</sup> <sup>1</sup>Mail Code ST, NASA Johnson Space Center, 2101 NASA Parkway, Houston, TX 77058, kevin.righter-1@nasa.gov; <sup>2</sup>Dept. of the Geophysical Sciences and <sup>3</sup>GSECARS, University of Chicago, 5734 S. Ellis Ave., Chicago, IL 60637.

**Introduction:** Spinel can be a significant host phase for V as well as other transition metals such as Ni and Co. However, vanadium has multiple oxidation states  $V^{2+}$ ,  $V^{3+}$ ,  $V^{4+}$  or  $V^{5+}$  at oxygen fugacities relevant to natural systems. We do know that D(V) spinel/melt is correlated with V and  $TiO_2$  content and  $fO_2$ , but the uncertainty of the oxidation state under the range of natural conditions has made elusive a thorough understanding of D(V) spinel/melt. For example,  $V^{3+}$  is likely to be stable in spinels, based on exchange with Al in experiments in the  $CaO-MgO-Al_2O_3-SiO_2$  system [1]. On the other hand, it has been argued that  $V^{4+}$  will be stable across the range of natural oxygen fugacities in nature [2,3]. In order to gain a better understanding of D(V) spinel/melt we have equilibrated spinel-melt pairs at controlled oxygen fugacities, between HM to NNO, where V is present in the spinel at natural levels (~300 ppm V). These spinel-melt pairs were analyzed using micro-XANES at the Advanced Photon Source at Argonne National Laboratory. The new results will be used together with spinel compositional data (Ti, V content) and oxygen fugacity, to unravel the effects of these variables on D(V) spinel/melt.

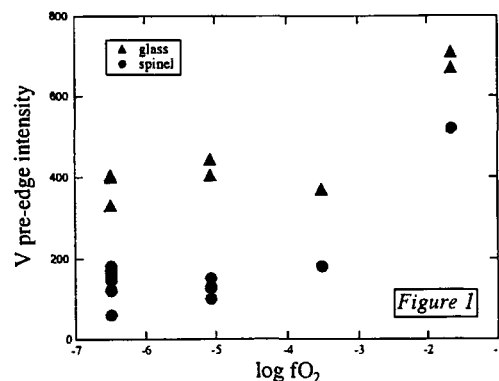
**Experimental:** A Hawaiian ankaramite was doped with 1% each of Cr, Ni and Ru or Cr, Rh and Os. These compositions were placed in 3 mm AuPd capsules and crimped (but not welded) at the top. These capsules were then welded, together with a buffer mixture in a separate alumina crucible, into an evacuated silica tube. Buffers used were hematite-magnetite (HM),  $MnO-Mn_3O_4$  (MNO),  $Re-ReO_2$  (RRO), and  $Ni-NiO$  (NNO), covering ~5.5  $\log fO_2$  units at 1300 °C. The silica tubes were held in the hotspot of vertical 1 atm furnaces for 48 hrs., and then quenched by rapid removal from the furnace. All runs contain spinel, glass, and Ru or RhOs metal; full details of these experiments were reported by [4].

**Synchrotron Micro-XANES spectroscopy (SmX):** Measurements of the valence of V were made using synchrotron micro-XANES (X-ray Absorption Near-Edge Structure) spectroscopy, at the Advanced Photon Source (APS), Argonne National Laboratory (beamline 13-ID, the Consortium for Advanced Radiation Sources or CARS). SmX measurements are made by focusing a monochromatic (cryogenic, Si (111) double crystal monochromator) X-ray beam from the synchrotron onto a spot on the sample and measuring the fluorescent X-ray yield from that spot as a function of incident X-ray energy. Synchrotron XANES spectroscopy can resolve small energy differences since the energy of the incident X-ray beam used to excite K- absorption edges can be controlled with resolution of ~0.1eV. Changes of fluorescent X-ray intensity and energy as the energy of the monochromatic incident beam is increased across an absorption edge are a function of oxidation state and coordination (e.g., [5]).

The oxidation states of V have been inferred using this technique on a range of planetary materials [6,7].

**Results:** Micro-XANES spectra, including well defined pre-edge peaks, were obtained on experimental spinels and glasses containing between 70 ppm and 2 wt% V, and in areas as small as  $5 \times 5 \text{ m}^2$ . Spinel grown at oxygen fugacities between NNO and MNO (three lowest  $fO_2$ s of this study) all have similar pre-edge intensities, but spinel grown at HM has a much higher intensity (Fig. 1). Glasses in all cases have higher pre-edge intensities than the spinel. Application of the glass calibration results of [8] to the glass pre-edge intensities indicates that the three lowest  $fO_2$  glasses are dominated by  $V^{4+}$ , while the highest  $fO_2$  glass (HM) contains mixed valence of 4+ and 5+. Although measurements on spinels of known V oxidation state are required to calibrate these spinel spectra in terms of oxidation state, the glass calibration of [8] provides some preliminary insight (particularly appropriate if V in spinel resides in octahedral sites). In this case, the results suggest  $V^{3+}$  dominance except for the most oxidized system (HM) which is inferred to be dominated by  $V^{4+}$ . However, the similar spectra for glass and spinel in the HM runs must be confirmed with additional measurements. These results show that V oxidation states can be determined using micro-XANES. Future plans include characterization of spinels with known V oxidation state, as well as experimental spinel-melt pairs at lower  $fO_2$ 's.

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# Testing the Magma Ocean Hypothesis Using Metal-Silicate Partitioning of Te, Se and S

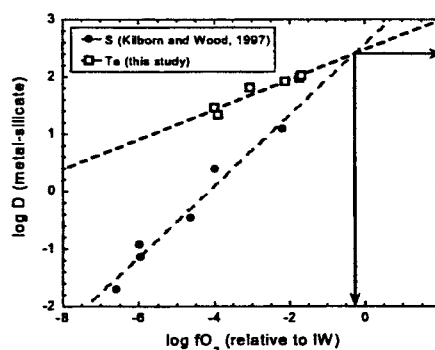
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**Introduction:** It has been observed that Te, Se and S all have similar depletions in the bulk silicate Earth ( $D_{\text{core-silicate Earth}} \sim 100$ ; [1]). If the core formed as a result of high P-T equilibrium at the base of a magma ocean, this equivalent depletion signature would require similar metal-silicate partitioning. The partitioning behavior of these elements is most certainly controlled by oxygen fugacity ( $fO_2$ ) (e.g. [2]), but to different extents. A powerful test of the magma ocean theory is to determine if these elements converge to the same D at a set of P-T- $fO_2$  conditions reasonable for core formation.

**Experimental Technique:** A series of high pressure (1-3 GPa), high temperature (1500-2000°C) metal-silicate partitioning experiments are being performed in a piston cylinder apparatus. Small amounts of Te or Se (1wt%) are added to a 50:50 mixture of powdered silicate melt and metal (Fe-Ni-Si), which is encapsulated in pre-densified MgO crucibles. The assembly is encased in a graphite furnace and BaCO<sub>3</sub> sleeve. Oxygen fugacity is varied by adding different amounts of Si to the metal phase. This alters the relative activities of Fe (in the alloy) and FeO (in the silicate melt), thereby changing the experimental  $fO_2$  relative to the iron-wüstite (IW) equilibrium. Samples are first pressurized and then heated to the experiment T at 100°C/minute, with T monitored using a W-Re thermocouple located directly above the sample. Experiments last 30 minutes and are rapidly quenched by cutting the power supply. After extraction, samples are mounted and sectioned in preparation for EMPA analyses.

**Results and Discussion:** Partitioning data for Te (this work) and S [2] at 2.5 GPa and 1700°C are shown in the accompanying figure. Both  $D_{\text{Te}}$  and  $D_{\text{S}}$  increase with  $fO_2$ , and importantly, each with different slope. The stronger  $fO_2$  dependence of  $D_{\text{S}}$  suggests this element is dissolved within the silicate melt in a different valence state (probably 2-) compared with Te (probably 1-). The trends converge at  $D = 250$  and  $\log fO_2 = \text{IW}-0.25$ . The Ds at convergence are much higher than those estimated from silicate mantle depletion ( $D_{\text{Te}} = 71$ ,  $D_{\text{S}} = 76$ ; [1]). Results thus far however, are from experiments run at relatively low P and T compared to estimated conditions of core formation. Changing both parameters to relevant conditions may alter both the magnitude and slope for the elements studied, and therefore alter the point of intersection.

Several studies have examined the effect of P and T on metal-silicate partitioning with different trends emerging for different elements. Factors affecting D include valence state, coordination within the silicate melt, and thermodynamic properties such as  $\Delta H_f$  and  $\Delta S_f$  [3,4].  $D_{\text{Ni}}$ ,  $D_{\text{Co}}$  and  $D_{\text{Mo}}$  were shown to decrease with increasing pressure and temperature, whereas  $D_{\text{Mn}}$  and  $D_{\text{V}}$  increased [5-9]. Ga and Re were found to favor the silicate phase with increasing temperature whereas P became more siderophile [10,11]. Importantly to this study,  $D_{\text{S}}$  has been shown to increase by an order of magnitude ( $10^2$  to  $10^3$ ) when P increased from 2.5 to 20 GPa [7]. Te and Se may therefore become more siderophile with pressure if they behave similarly.



From estimates of their depletion in the silicate Earth [1], it is clear that Te, Se, and S behave similarly during metal-silicate partitioning. We have found that Te and S partition into the metal phase by an equal amount close to the IW buffer, yet with a much higher D than predicted. Although such results are incompatible with the magma ocean model, increased T may lower Ds to the required level, although the effect of P could counter this. Experiments are currently in progress to assess these effects.

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**SOLUBILITY OF OXYGEN IN LIQUID IRON AT HIGH PRESSURE AND CONSEQUENCES FOR THE EARLY DIFFERENTIATION OF EARTH AND MARS.** D.C. Rubie<sup>1</sup>, C.K. Gessmann<sup>1,2</sup> and D.J. Frost<sup>1</sup>,  
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**Introduction:** Knowledge of the solubility of oxygen in liquid iron alloy at high pressure is necessary for determining if oxygen is present as a major light element in planetary cores. In addition, solubility measurements enable the partitioning of oxygen between metal and silicates to be determined which can then be used to constrain oxygen fugacity during core formation, based on a given bulk composition.

**Experimental Results:** We have determined oxygen solubility experimentally as a function of pressure (9-18 GPa), temperature (2173-2673 K) and oxygen fugacity (1.1 to 3.6 log units below the iron-wüstite buffer) in samples of liquid Ni-Fe alloy contained in magnesiowüstite capsules using a multianvil apparatus [1]. Results show that solubility increases as a function of oxygen fugacity ( $fO_2$ ) and temperature, with the maximum solubility determined in this study being 1.28 wt%. In order to determine the effect of pressure independently of oxygen fugacity, we calculate the distribution coefficient,  $K_D$ , for the partitioning of oxygen between liquid Fe-alloy and magnesiowüstite:

$$K_D = \frac{X_O^{met} X_{Fe}^{met}}{X_{FeO}^{mw}}$$

where  $X_O^{met}$ ,  $X_{Fe}^{met}$ , and  $X_{FeO}^{mw}$  are the mole fractions of oxygen in metal, Fe in metal and FeO in magnesiowüstite respectively.  $K_D$  includes the term  $X_{Fe}^{met} / X_{FeO}^{mw}$  and is therefore independent of  $fO_2$ . The distribution coefficient, and therefore oxygen solubility at constant  $fO_2$ , decreases with increasing pressure. In order to extrapolate the oxygen solubility data to higher pressure ( $P$ ) and temperature ( $T$ ), we use the relationship

$$RT \ln K_D = -\Delta H + T\Delta S - P\Delta V$$

to fit our results, together with those of an earlier study [2], where  $\Delta H$ ,  $\Delta S$  and  $\Delta V$  are changes in enthalpy, entropy and volume respectively for the oxygen exchange reaction and  $R$  is the gas constant. Based on a simple extrapolation of the solubility results (constant values of  $\Delta H$ ,  $\Delta S$  and  $\Delta V$ ), oxygen solubility reaches 5-15 wt% at 3500-4000 K, moderate pressures (e.g. 5-10 GPa), and an oxygen fugacity 2 orders of magnitude below the iron-wüstite buffer. However, as pressure exceeds ~40 GPa, oxygen solubility is predicted to become low, even at very high temperatures.

**Core Formation Model:** Using the simple extrapolation of oxygen solubility to high pressures and temperatures, we have modelled the geochemical consequences of metal-silicate separation in magma oceans

and can thus explain why the FeO content of the Earth's mantle (~8 wt%) is much lower than that of the Martian mantle (~18 wt%) [1]. We assume that both Earth and Mars accreted from material with a chondritic composition. Because the initial oxidation state is uncertain, we vary this parameter by defining different initial oxygen contents. The geochemical consequences of metal-silicate separation are determined using a simple fractionation model and we assume that the temperature at the base of the magma ocean is close to the peridotite liquidus. In the case of Earth, high temperatures in a magma ocean with a depth >1200 km result in significant quantities of oxygen dissolving in the liquid metal with the consequent extraction of FeO from the residual silicate. In contrast, on Mars, even if the magma ocean extended to the depth of the current core-mantle boundary, temperatures are not sufficiently high for oxygen solubility in liquid metal to be significant. The results show that Earth and Mars could have accreted from similar material, with an initial FeO content of around 18 wt%. On Earth, oxygen was extracted from silicates by the segregating metal during core formation, leaving the mantle with its present FeO content of ~8 wt%. On Mars, in contrast, the segregating metal extracted little or no oxygen and left the FeO content unaltered at ~18 wt%. A consequence of this model is that oxygen could be an important light element in the Earth's core but not in the Martian core.

On Earth, as metal migrates to greater depths below the base of the magma ocean, the solubility of O is predicted to decrease strongly, which could lead to precipitation of FeO and the enrichment of the lower part of the mantle in this component. Alternatively, if all or part of the dissolved oxygen is transported to the core (e.g. as a disequilibrium component), the consequences could include the presence of significant amounts of oxygen as a light element in the core and/or the formation of a FeO-rich layer at the CMB due to exsolution of the excess oxygen. In order to clarify these issues, oxygen solubility measurements at much higher pressures (e.g. 30-100 GPa) are required.

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**METALLIC LIQUID SEGREGATION IN PLANETESIMALS.** T. Rushmer<sup>1</sup> and N. Petford<sup>2</sup>, <sup>1</sup>University of Vermont (Department of Geology, Burlington, VT 05405; Tracy.Rushmer@uvm.edu), <sup>2</sup>Centre for Earth and Environmental Sciences (Kingston University, Kingston Upon Thames, Surrey, UK; N.Pet@kingston.ac.uk)

**Introduction:** Segregation of Fe-Ni-S-O liquids during partial melting of chondritic parent material imparts a distinct geochemical signature on the composition of residual metal and helps determine siderophile partitioning behavior [1]. Chemical signatures will vary according to initial parent body composition, physical segregation mechanisms and at what degree of partial melting core-forming liquids are extracted. In this study, geochemical data from deformation experiments performed on partially molten ordinary chondrite (Kernouve) have been collected on Fe-S-Ni-O quench and associated Fe-Ni residual metal by electron probe and LA-ICPMS [2]. Siderophile concentrations in the quench liquid and associated metal, dynamically segregated at different degrees of partial melting, were used to calculate partition coefficients for different solid metal/liquid metal compositions and are reported in [3]. Deformation in segregating liquid metal from silicate most likely plays a more important role in core formation than previously thought and here we present experimental results and a model which drives segregation by pressure gradients developed in the silicate matrix undergoing porous flow and pure shear [4]. The model also provides estimates of segregation rates. Combined with the geochemical data, possible links between liquid fraction chemistry and rate of transport may be made.

**Experimental Results:** Four experiments were chosen for in-depth chemical analyses. Analyses provided data on both solid metal and quench Fe-S-Ni-O compositions in Kernouve experiments (KM) [3]. The experiments chosen were: KM-12 at the lowest degree of partial melting (P=1.2 GPa, T=900°C, strain rate=10<sup>-6</sup>/s, no silicate melt present, 10% strain, < 5 vol% quench metallic liquid present). KM-12 quench liquid has S contents of 30-32 wt% and O contents 0.24-0.66. KM-10 at a moderate degree of partial melting (P=1.0 GPa, T=925°C, strain rate=10<sup>-3</sup>/s, 40% strain, 5-10 vol% quench metallic liquid). KM-10 quench Fe-S-Ni-O located in high stress shear domains had S contents of 26-29 wt% and O between 0.04-0.23. KM-17 (P=1.2 GPa, T=940°C, strain rate=10<sup>-6</sup>/s, 10% strain, 15-20 vol% quench metallic liquid and ~12% silicate melt present, moderate degree of partial melting). KM-17 S quench liquid contents range between 15 and 20 wt% and O from 0.2 to 1.1. KM-11 (P=1.0 GPa, T=990°C, strain rate=10<sup>-3</sup>/s, 15% strain, > 25 vol% quench metallic liquid, 15-18% silicate melt; highest degree of partial melting). KM-11 quench liquid S contents range between 8 and 12 wt% S and O

between 1.0-2.1 wt%. Calculated D values (SM/LM) show excellent agreement with equilibrium solid metal-liquid metal partition coefficients determined in S-bearing systems [6]. Both studies show the influence of S on siderophile partitioning, with the higher S content, low volume quench liquid having Ds>200 for highly siderophile elements and Ds closer to 1 for the highest volume, lowest S content metallic liquid [3,6]. The role of O needs to be further considered, but as shown by [7] may be significant in porous flow segregation models. We can estimate the rate of Darcy flow (steady seepage) as a function of porosity and using the compositions of the liquid metal fraction, begin to link major element and siderophile chemistry to flow rates. We model a 100-km planetesimal body undergoing Darcian flow and discuss rates of segregation induced by deformation-enhanced flow.

**Melt Segregation Model:** The shear dilatancy model mathematically describes a porous matrix that is modified by deformation to create dilatancy (low pressure sites) and drives melt segregation [4]. Using the permeability relationship from [5], calculations of the rates of flow in a porous medium can be initially made (porosity = melt fraction). The melt flow is given in m/s (Darcy velocity) and ranges between 10<sup>-8</sup> m/s to 10<sup>-7</sup> m/s for porosities (liquid fraction) of 0.05 to 0.10. As porosity increases, flow rates increase, but level off to a range between 10<sup>-5</sup> m/s to 10<sup>-4</sup> m/s for porosities of 0.40 to 0.50. When deformation events are included, calculated shear-induced flow velocities range from 10<sup>-7</sup> to 1 ms<sup>-1</sup> for strain rates up to 10<sup>-3</sup> s<sup>-1</sup>. At higher rates, compatible with catastrophic impact, instantaneous flow velocities may exceed 10 ms<sup>-1</sup>. Transport of metallic liquids with a range of S contents may be possible by deformation-enhanced flow, in tandem with background percolation of low melt fraction-high S+/-O bearing liquids. These initial results suggest that bodies of comparable size subjected to periods of deformation should have formed proto-cores before accreting to form larger terrestrial bodies if subjected to deformation at strain rates in excess of 10<sup>-8</sup> s<sup>-1</sup>.

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**OXYGEN FUGACITY OF LUNAR BASALTS AND THE LUNAR MANTLE. RANGE OF  $fO_2$  AND THE EFFECTIVENESS OF OXYBAROMETERS.** C.K. Shearer and J.J. Papike. Institute of Meteoritics, Department of Earth and Planetary Sciences, University of New Mexico, Albuquerque, N.M. 87131.

**Introduction:** Estimates of  $fO_2$  for mare basalts and the lunar mantle have been made using a variety of approaches: intrinsic  $fO_2$ , mineral assemblages, melt and mineral compositions and the oxidation state of multiple valence cations. Although each approach has its limitations, most indicate that mare basalts crystallized at  $fO_2$  between the iron-wüstite buffer (IW) and the ilmenite breakdown reaction [i.e. 1-4]. It has also been inferred from these estimates that the lunar mantle is also highly reduced lying at conditions below IW. Here, we illustrate some of the recorders of  $fO_2$  in lunar basalts and the implications for the lunar mantle.

**Mineral Assemblage:** To a first approximation, the presence of metallic iron or Ni,Fe alloys in mare basalts indicates that they crystallized at  $fO_2$  conditions below the iron-wüstite buffer. The metal-melt equilibria and the Cr content of the olivine (+spinel) were interpreted as indicating a pre-eruptive  $fO_2$  of IW-1.3 for the lunar picritic glasses [4]. Some lunar basalts show textural and mineralogical evidence for further subsolidus reduction. Reported subsolidus reactions such as ulvöspinel ilmenite + metallic iron and fayalite cristobalite + metallic iron take place at a range of  $fO_2$  below both IW and FIQ buffers.

**Intrinsic  $fO_2$ :** Intrinsic  $fO_2$  measurements and thermodynamic gas equilibria calculations show that the range of temperature and  $fO_2$  for mare basalt crystallization are relatively small, varying from  $10^{-13}$  at 1200 C to  $10^{-16}$  at 1000 C [1-4]. Relative to standard buffer curves, these values are approximately 0.2 to 1.0 log units below iron-wüstite (IW) and above the univariant curve that defines the stability of ilmenite.

**Mineral Compositions:** Mineralogical observations such as the total absence of ferric iron in both silicates and oxides and the presences of reduced valence states of Cr and Ti [5] are consistent with the above observations. The composition of spinels in basalts has been shown to partially reflect  $fO_2$  [5,6,7]. The spinel crystallization trajectories are consistent with conditions below IW. Differences in spinel compositions have not been related to differences in  $fO_2$  among lunar basalts.

**Basalt Compositions:** The FeO content of the lunar basalts has been interpreted [8] as indicating that the mare basalts were generated at  $fO_2$  of IW-1. The Cr content of liquids coexisting with spinel varies considerably with  $fO_2$ , such that Cr is low (< 1000 ppm) at FMQ and high (>2700 ppm) at IW [9]. This is due to  $Cr^{2+}$  being less soluble in spinel in the mantle at reducing conditions and therefore remaining in the melt.

The Cr content of primitive lunar basalts (2700–6300 ppm) is significantly higher than similar terrestrial basalts (<1500 ppm). Therefore, if spinel was a residual phase in the lunar mantle and the Cr content was near chondritic, the high Cr content of the mare basalts suggests a reduced lunar mantle [9,10].

**Multiple Valence Cations:** Reduced valences of oxidation cation pairs appear to be common in lunar basalts. For example, the existence of divalent Eu and Cr, trivalent V, and even trivalent Ti have been documented in mare basalts. The ratio of oxidized species to reduced species provides a potential quantitative tool for determining  $fO_2$ . The ratio of  $(Eu/Gd)_{plag}/(Eu/Gd)_{pyx}$  in mare basalts and highland plutonic rocks although somewhat different indicate  $fO_2$  at IW-1 or slightly more reducing. Vanadium valence for the lunar volcanic glasses ranges from 2.7 to 2.9. These values are substantially lower than measurements made on terrestrial basaltic glasses (3.7-4.2) [11]. Using the V valence in these basaltic glasses reflect a range of  $fO_2$  from IW-1 to IW-2.2 [11].

**Discussion:** Many oxybarometers have been used to estimate the  $fO_2$  of lunar basalts. Estimates for lunar basalts range from IW-0.4 to IW-2.2. Do these reducing conditions reflect reducing crust and mantle environments or reduction processes during magma transport and eruption? Proposed mechanisms for the eruption of the lunar picritic glasses require the reduction of the magma via the oxidation of graphite (i.e.  $Cr_2O_3 + C \rightarrow 2CrO + CO$ ). Such a reaction is also suggested by metal droplets in some of the glasses. However, there does not appear to be a significant difference in reduced species/oxidized species in these glasses [11] nor do the proposed reactions result in a dramatic change in the  $fO_2$  of the basaltic melt. An interesting observation is the difference in mare basalts and parental basalts to the magnesian-suite that were emplaced in the lunar crust prior to mare magmatism. Preliminary results indicate that the magnesian-suite magmas had lower Cr, Ni, and Co and higher  $(Eu/Gd)_{plag}/(Eu/Gd)_{pyx}$  than the mare basalts. Whether this is simply a product of different source regions or different  $fO_2$  needs to be investigated further.

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**THERMODYNAMIC STUDY OF DISSOCIATION PROCESSES OF MOLECULAR OXYGEN IN VAPOR OVER OXIDE COMPOUNDS.** S. I. Shornikov, Centre of Isotopic Research, Karpinsky All-Russian Geological Institute, Sredny pr., 74, Saint-Petersburg, 199106, Russia. E-mail: sergey\_shornikov@vsegei.ru.

**Introduction:** The study of evaporation and condensation processes of substance has attracted considerable interest for understanding of the problems relating to the chemical evolution of protoplanet substance in the process of successive condensation of incandescent gases at forming space objects as physicochemical systems. Recently we observed the linear dependence of logarithm of vapor total pressure over the  $\text{CaO-MgO-Al}_2\text{O}_3\text{-SiO}_2$  compounds vs. the molecular oxygen content in vapor (or the degree of its dissociation) [1]. It points to the fact that there is a relationship between the red-ox reactions in the gaseous substance and the condensation processes. In this connection it seems to be useful to consider the observed regularities on example of another oxide compounds.

**Calculations:** In the present study the composition and partial pressures of 305 vapor species along with the total pressures over 198 most investigated oxides and its compounds were calculated in terms of thermodynamic approach for the temperature range 1700-2200 K using the own experimental and reference data on the constants of gas-phase and heterogeneous equilibria and the oxide activities in oxide compounds [2-7]. The choice of the study temperature range was caused by the condensation temperatures of most important compounds formed at cooling of substance in the solar nebula. The total vapor pressure over oxide compounds were calculated by summing over the proper partial pressures of the vapor species taken for the case of chemically neutral conditions.

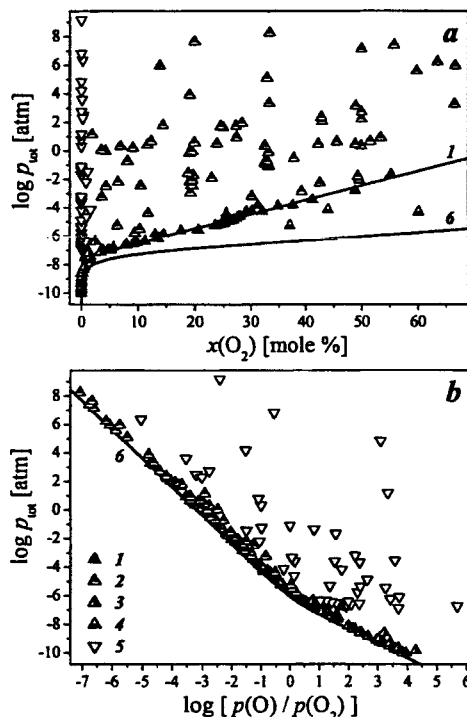
**Results and Discussion:** Some obtained data are presented in Figures. As may be seen from Fig. one can subdivide oxides and its compounds into two main groups with respect to the dissociation degree of the molecular oxygen in vapor.

The first group (1-4) is characterized by the different content of molecular oxygen in vapor and the atomic-to-molecular oxygen ratio being the same as in the case of pure oxygen (6). A number oxide compounds ( $\text{Al}_2\text{O}_3$ ,  $\text{CaO}$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{MgO}$ ,  $\text{SiO}_2$ , etc.) denoted (1) in Fig. possess the minimal total vapor pressure at maximal molecular oxygen content in vapor. The minimal molecular oxygen content in vapor have  $\text{BeO}$ ,  $\text{Ce}_2\text{O}_3$ ,  $\text{HfO}_2$ ,  $\text{Tb}_2\text{O}_3$ ,  $\text{ZrO}_2$ , etc. denoted (3) in Fig.

The significant dissociation of the molecular oxygen in vapor ( $x(\text{O}_2) < 1$  mole %) is typical for the second oxide group ( $\text{B}_2\text{O}_3$ ,  $\text{BaO}$ ,  $\text{H}_2\text{O}$ ,  $\text{MoO}_3$ ,  $\text{NbO}$ ,  $\text{NbO}_2$ ,  $\text{P}_4\text{O}_{10}$ ,  $\text{Pu}_2\text{O}_3$ ,  $\text{Re}_2\text{O}_7$ ,  $\text{Rh}_2\text{O}_3$ ,  $\text{SO}_3$ ,  $\text{ThO}_2$ ,  $\text{Ti}_2\text{O}_3$ ,  $\text{U}_3\text{O}_8$ ,  $\text{V}_2\text{O}_5$ ,  $\text{WO}_3$ , etc.), which denoted (5) in the Fig.

The suggested oxide classification based on the molecular oxygen dissociation degree gives an opportunity to make some conclusions on the general features of the condensation processes and provides rather accurate estimations of the total vapor pressures over oxide compounds.

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**Figures:** The total vapor pressure over oxide compounds vs. molecular oxygen content (a) and ratio of partial pressures of atomic and molecular oxygen (b) in vapor at 2000 K (see text for explanation).

## **Oxygen Profile of a Thermo-haliophilic Community in the Badwater Salt Flat.**

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Badwater is the lowest, saltiest, and hottest, place in North America. This extreme environment is 86 meters (282 feet) below sea level surrounded by four mountain ranges. Due to the geographical location Badwater does not receive moisture from the prevailing winds, this intern results in a hot, arid, and salty environment. Despite these extreme living conditions, microbes manage to flourish within the salt flat. The salt acts as an insulator making life just beneath the surface more comfortable. In this paper, we compare the microbial population versus oxygen concentration; and the importance of and the role of oxygen in metabolic functions by these thermo-haliophiles. Furthermore a model of the oxygen profile will also provide an insight to the oxygen cycle in salty environments. This research has implications for the limits of life on Earth and Mars. Recent results from the MER rovers show that water on Mars was very salty. Measuring the oxygen profile in these salty environments on Earth provides a framework within which potential life on Mars can be evaluated. The use of an oxygen profile could also be used as a search criteria for life.

**OXYGEN BAROMETRY USING SYNCHROTRON MICROXANES OF VANADIUM.** S.R. Sutton<sup>1,2</sup> (sutton@cars.uchicago.edu), J.M. Karner<sup>3</sup>, J.J. Papike<sup>3</sup>, J. S. Delaney<sup>4</sup>, C.K. Shearer<sup>3</sup>, M. Newville<sup>2</sup>, P. Eng<sup>2</sup>, M. Rivers<sup>1,2</sup>, and M. D. Dyar<sup>5</sup> <sup>1</sup>Department of Geophysical Sciences and <sup>2</sup>Consortium for Advanced Radiation Sources, University of Chicago, Chicago, IL 60637; <sup>3</sup>Institute of Meteoritics, Department of Earth and Planetary Sciences, University of New Mexico, Albuquerque, NM 87131-1126; <sup>4</sup>Geology Department, Rutgers University, New Brunswick, NJ 08903; <sup>5</sup>Department of Earth and Environment, Mount Holyoke College, South Hadley, MA.

A promising proxy for oxygen fugacity is the valence of vanadium because it has a large number of possible valence states in nature (2+, 3+, 4+ and 5+) and is ubiquitous in earth and planetary materials. A new, non-destructive method for valence determinations of vanadium and oxygen fugacity estimates with spatial resolution of a few micrometers is synchrotron x-ray absorption near edge structure (XANES) spectroscopy [1-3].

In XANES spectroscopy, the x-ray absorption edge of the element of interest is mapped with high energy resolution. Typically, the XANES spectrum is obtained by measuring the intensity of a characteristic fluorescence line (in this case, V K<sub>α</sub>) as the incident x-ray energy is scanned over the appropriate absorption edge. The valence determination uses a pre-edge peak near 5470 eV interpreted to be due to a dipole-forbidden, 1s-3d electron transition [4]. The intensity (and energy) of this peak increases systematically as valence becomes more oxidized. Intensity values are normalized to the "above edge" intensity, defined to be 1000. Vanadium K XANES spectra were measured using the undulator-based microprobe at Sector 13 (GeoSoilEnviroCARS) at the Advanced Photon Source, Argonne National Laboratory [5].

Five suites of experimental glasses of basaltic or komatiitic composition with ~1% V<sub>2</sub>O<sub>5</sub> dopant were studied for valence and oxygen fugacity standardization purposes: *Schreiber suite* (H. Schreiber, Virginia Military Inst): FAD and FAS composition [6] 1500 °C at log *f*O<sub>2</sub> from 0 to -9. V valences (V<sup>5+</sup> to V<sup>3+</sup>) were previously obtained independently by optical spectrometry. *Hanson suite* (B. Hanson, Corning Glass; J. Jones, NASA-JSC): FAD composition [7], 1310 or 1320 °C at *f*O<sub>2</sub> from air to the Cr-CrO buffer. *Canil suite* (D. Canil, University of Victoria, Canada): Komatiitic composition [8]; 1225 to 1425 °C at log *f*O<sub>2</sub> from -5.5 to -10.7. *Beckett suite* (J. Beckett, Cal. Inst. Tech.): CMAS composition; an isobaric experiment (log *f*O<sub>2</sub> = -8), 1274 to 1425 °C. *Karner suite* (J. Karner, U. New Mexico): Lunar green and orange glass composition; log *f*O<sub>2</sub> = IW +1 to -2, 1430 °C.

A plot of vanadium pre-edge peak intensity versus known valence state for the Schreiber glasses shows a well-defined trend. Using this calibration curve, the effective valences of other glasses can be determined.

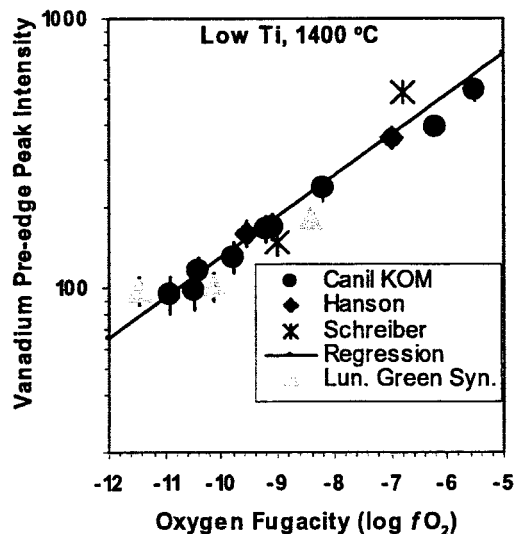
The Beckett suite and several of the Hanson samples represent isobaric couples that were used to determine the magnitude of valence variations due to temperature differences. The fractional intensity change per degree was found to be  $-0.0027 \pm 0.0002$ .

In this way, a calibration curve for peak intensity vs. oxygen fugacity can be produced for liquidus temperature of each unknown. Increased basicity of the melt leads to increased valence of a redox couple [6] and work is in progress to quantify this effect on vanadium valence. A "calibration curve" for low Ti standard glasses at 1400 °C is shown in Figure 1.

Because site geometry can also affect pre-edge peak intensity, we make the implicit assumption that changes in coordination in basaltic glasses occur in unknowns in an analogous way to those in the standards. MicroEXAFS data for both natural and synthetic glasses support this assumption and can be satisfactorily interpreted within a coordination sequence involving octahedral coordination of V for valences between V<sup>3+</sup> and V<sup>4+</sup> with smaller coordination numbers becoming dominant for oxidized samples between V<sup>4+</sup> and V<sup>5+</sup>.

The vanadium redox system is a robust oxybarometer. Further work is in progress to improve our understanding of the effects of melt composition and temperature.

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**Figure 1:** Pre-edge peak intensity versus oxygen fugacity for standard glasses after temperature correction to 1400 °C.

**MASS-INDEPENDENT ISOTOPIC FRACTIONATION OF SULFUR FROM SULFIDES IN THE HURONIAN SUPERGROUP, CANADA.** S. Tachibana<sup>1</sup>, T. Hirai<sup>1</sup>, K. Goto<sup>1</sup>, S. Yamamoto<sup>1</sup>, J. L. Kirschvink<sup>2</sup>, R. E. Kopp<sup>2</sup>, N. Ohkouchi<sup>3</sup>, Y. Isozaki<sup>4</sup>, R. Tada<sup>1</sup>, E. Tajika<sup>1</sup>, N. T. Kita<sup>5</sup> and Y. Morishita<sup>5</sup>, <sup>1</sup>Dept. of Earth and Planet. Sci. (Bldg. 1), Univ. of Tokyo, 7-3-1 Hongo, Tokyo, 113-0033, Japan (tachi@eps.s.u-tokyo.ac.jp), <sup>2</sup>Division of Geological and Planetary Sciences, California Institute of Technology, Pasadena, CA 91125, USA, <sup>3</sup>Institute for Frontier Research on Earth Evolution, 2-15, Natsushima, Yokosuka 237-0061, Japan, <sup>4</sup>Dept. of Earth Science and Astronomy, Univ. of Tokyo, 3-8-1 Komaba, Meguro, Tokyo 153-8902, Japan, <sup>5</sup>Geological Survey of Japan, AIST Tsukuba Central 7, Tsukuba 305-8567, Japan.

Mass-independent isotopic fractionation (MIF) in sulfur isotopes from sedimentary rocks older than 2.47 Gyr has been attributed to the low oxygen content of the atmosphere [e.g., 1-3]. The recent finding of near-zero MIF of sulfur in pyrites from ~2.32 Ga shales of the Rooihooite and Timeball Hill formations, South Africa, suggests that atmospheric oxygen may have reached ~10<sup>-5</sup> PAL by 2.32 Ga [4].

The Huronian Supergroup of Canada was deposited between 2.45-2.22 Ga, possibly overlapping with deposition of the Rooihooite and Timeball Hill Formations, and preserves a record of three glaciations. Small MIF of sulfur ( $\delta^{33}\text{S} < 0.5\%$ ) has been reported for sulfides from the Huronian Supergroup (McKim, Ramsay Lake, and Pecors Formations) [5]. We have started in-situ analyses of the sulfur isotopic compositions of sulfides for formations overlying those reported by [5], including the second and third glacial diamictites (Bruce and Gowganda Formations), using the Cameca ims-1270 ion microprobe at the Geological Society of Japan. Some sulfides are rounded, and some are aligned parallel to lamination, which implies that they are of detrital origin.

Our preliminary analyses show that sulfides from Pecors, Missisagi, Bruce, Espanola, Gowganda, and Gordon Lake Formations appear to have  $\delta^{33}\text{S}$   $\delta 0.3\%$ , consistent with [5]. Except in the youngest formation, the Gordon Lake Formation,  $\delta^{34}\text{S}$  is less than +4%. The low  $\delta^{33}\text{S}$  (<0.3%) implies that either oxygen levels had increased by Huronian time, or that the Huronian was characterized by enhanced, glacially-driven mixing of S reservoirs. The relatively low  $\delta^{34}\text{S}$  of formations underlying Gordon Lake Formation may indicate a sulfate content of <200  $\mu\text{M}$  during deposition of those formations [6], while the increase in  $\delta^{34}\text{S}$  in the Gordon Lake Formation is consistent with other indicators of increased sulfate, including pseudomorphs after gypsum.

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**MASS INDEPENDENT ISOTOPES AND APPLICATIONS TO PLANETARY ATMOSPHERES. M. H. Thiemens. Department of Chemistry and Biochemistry, UCSD. La Jolla, CA 92093-0356**

**Introduction:**

With the discovery of the mass independent isotopic fractionation process by Thiemens and Heidenreich in 1983, a new technique to understand various natural processes became available. Since that time, a quantum mechanical basis for understanding this effect became available. This has strengthened the ability to understand how this unique fractionation process may occur in nature. It has now been demonstrated that for example, in the Earth's atmosphere, every oxygen bearing molecule, with the exception of water, is mass independently fractionated. The molecules include: CO, CO<sub>2</sub>, O<sub>2</sub>, O<sub>3</sub>, H<sub>2</sub>O<sub>2</sub>, N<sub>2</sub>O and solid aerosol nitrate and sulfate.

From ice core studies, the evolution of the oxidative capacity of the Earth has now been tracked and quantified on a > 100,000 year time scale. The analysis of sulfate and nitrates has provided a unique way to understand and quantify the alterations in the oxidative capacity of the earth. In addition, the measurements have lead to a highly specific quantification of oxidative processes and their chemical reaction mechanisms, e.g. relative roles of homegenous and heterogenous oxidation.

From oxygen isotopic analysis of secondary minerals from SNC meteorites, the interaction between the atmosphere and regolith has been resolved at a much higher degree of specificity. This work has shown that the record of the planetary processes may be captured in the isotopic record and maintained on billion year time scales.

In sum, the use of mass independent isoptic measurements has provided new details regarding a wide range of natural processes in the atmosphere, hdrospehere, and geosphere. In the future, such measurements will amplify understanding of planetary bodies, their interactions and evolution. Future return sample missions will additionally benefit from these measurements.

**ELECTRICAL CONDUCTIVITY, OXYGEN FUGACITY, AND MANTLE MATERIALS.** James A. Tyburczy, Department of Geological Sciences, Arizona State University, Box 871404, Tempe, AZ 85287-1404, jim.tyburczy@asu.edu.

**Introduction:** Knowledge of electrical properties of Earth materials under conditions of the Earth's interior can contribute to our understanding of the temperature profile of the interior, the phases present at depth, and, potentially, the chemical environment and oxygen fugacity of the interior. Electrical properties of rocks are generally strongly dependent on temperature, on oxygen fugacity, and on the presence (or absence) of highly conducting mineral phases, fluids or melts, or pathways [1-5]. Laboratory determinations of mineral conductivities have advanced sufficiently that it is now possible to compare conductivity models that include temperature and composition constraints with observed mantle conductivity profiles.

The point defect chemistry governing conductivity at low pressures in olivine is well constrained [6,7], with conductivity governed by ferric iron on a magnesium site (the 'small polaron'). Lateral conductivity variations at 200 km depth between continental shields and oceanic regions are about 1.5 log units. If the sole cause of this variation is oxygen fugacity, this implies a difference of 4-8 log units in oxygen fugacity between these regions. At 400 km depth, the difference of about 0.5 log units would be caused by a difference in oxygen fugacity difference of 2-3 log units, assuming small polaron hopping in olivine is the dominant conduction mechanism.

High pressure measurements been made on olivine, wadsleyite, ringwoodite, perovskite, and magnesiowustite under sufficiently controlled conditions to permit modeling of the transition zone and lower mantle [8-10]. Conductivity at depth is consistent with the sharp seismic boundaries corresponding to the olivine to wadsleyite to ringwoodite to perovskite transitions. Anhydrous wadsleyite and ringwoodite exhibit conductivities as much as two orders of magnitude greater than olivine of the same composition. With these results, it is possible to model mantle conductivities with models incorporating composition and temperature variations [9]. Detailed point defect models for these phases are not yet available; they are important for complete understanding of the process and extrapolation to conditions not easily studied in the lab, such as oxygen fugacity variations at very high pressures.

Hydrogen diffusion studies [11] suggest that olivine conductivity will be greatly enhanced by the presence of plausible mantle levels of hydrogen [12], and that the lattice preferred orientation dependence of hydrogen-enhanced conductivity will be much greater than that of dry olivine [13]. Preliminary data indicate

an increase in conductivity of wadsleyite with the addition of water, but the increase is smaller than predicted for olivine [14]. Details of the point defect chemistry of hydrogen in nominally anhydrous transition zone minerals remain to be resolved. The inferred conductivities of hydrogen-bearing olivine lead to interpretation of oceanic conductivity profiles as indicating the presence of H-rich sublithospheric mantle [4] and the interpretation of continental conductivity profiles as indicating that sub cratonic mantle is unusually dry [15].

For perovskite, lab high P conductivity measurements are consistent with inferred lower mantle conductivities [16]. Conductivity appears to be dominated by ionic conduction (oxygen vacancies) [16].  $\text{Al}^{+3}$  in perovskite stabilizes  $\text{Fe}^{+3}$  in the structure [17]. This may reduce the effect of oxygen fugacity on the conductivity in the lower mantle.

**Conclusion:** Significant progress has been made in determination of conductivities of mantle minerals at mantle pressure and temperature conditions with control of environmental conditions. Petrologic models of mantle conductivity can be made for comparison with observed conductivity profiles. Quantitative point defect models of high pressure phases and direct measurement of the influence of oxygen fugacity and hydrogen content on conductivity of nominally anhydrous minerals are needed for the proper interpretation of Earth electrical conductivity profiles in terms of the temperature and physical state of the mantle.

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# CRUSTAL EVOLUTION AND MATURATION ON EARTH: OXYGEN ISOTOPE EVIDENCE

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Zircon is a common accessory mineral in intermediate to felsic igneous rocks and also occurs in some mafic rocks. Zircons provide the most reliable record of magmatic oxygen isotope ratio as well as U-Pb age if significant radiation damage is avoided. No other mineral permits  $^{18}\text{O}(\text{magma})$  to be confidently determined and coupled to age of crystallization (1). Zoned magmatic zircons serve as time capsules, preserving isotopic, trace element and mineral/melt inclusion evidence of evolving magmatic conditions.

Igneous zircons of known age (3.6 Ga to 0.2 Ma) from Earth have been analyzed for  $^{18}\text{O}$  by laser fluorination at the University of Wisconsin from over 1100 rocks worldwide. In addition to laser analyses of zircon concentrates (1-3 mg), single detrital zircons (4.4 to 3.0 Ga) from the Jack Hills, Western Australia were analyzed in situ (30 micron spot, ~2 ng) by ion microprobe (2).

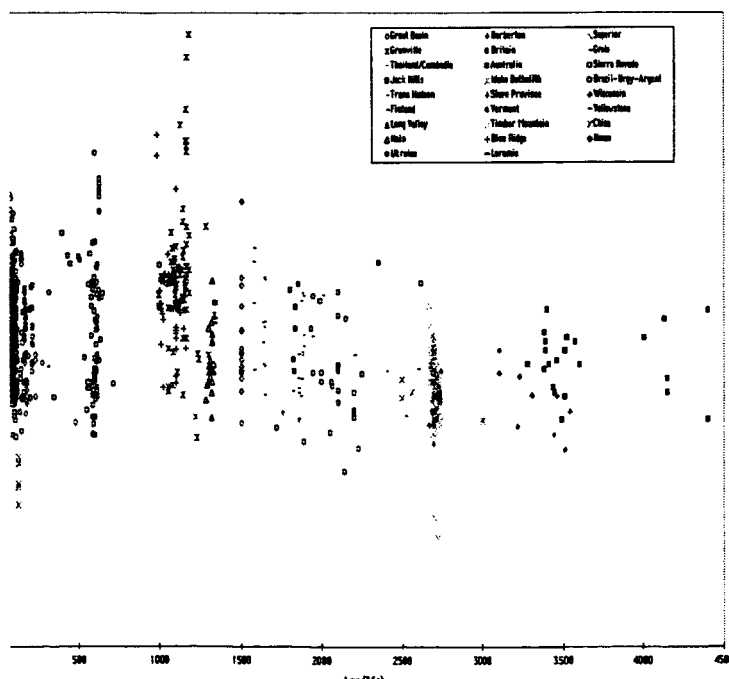
The range and variability of  $^{18}\text{O}$  in all Archean samples is subdued ( $^{18}\text{O}(\text{Zrc})=5$  to 7.5‰). Most samples have  $^{18}\text{O}=5\text{--}6.5\text{‰}$ , consistent with high temperature equilibrium with mantle values ( $\text{Zc}=5.3\pm0.3\text{‰}$ ) or mildly evolved composition. No magmatic zircons have been analyzed from the Archean with "S-type" values ( $^{18}\text{O}$  above 8‰). This includes samples from Superior Province (3.0 - 2.7 Ga), Lewisian (2.7 Ga), Slave Province (2.7 Ga), and Barberton (3.5 to 2.7 Ga). Zircons analyzed by ion microprobe from the Jack Hills are indistinguishable

in  $^{18}\text{O}$  from other Archean samples. The highest values (7.4‰) are interpreted to result from exchange of pre-magmatic protolith with surface water, even in the Early Archean zircons (4.4-4.0 Ga) (3).

Values of  $^{18}\text{O}(\text{Zc})$  from the Proterozoic and Phanerozoic are significantly more variable. Many zircons are above 8‰ showing that magmas with  $^{18}\text{O}(\text{WR}) > 9\text{--}10\text{‰}$  became common only after ~1.5 Ga. The increased variability of the oxygen isotope ratios of intermediate to felsic magmas occurs in the Middle Proterozoic. Since fractionation of oxygen isotopes to values higher than the mantle requires low temperatures where fractionation is large, the greater variability in  $^{18}\text{O}$  must reflect recycling of supracrustal lithologies and progressive maturation of the crust. The dominant sources of high- $^{18}\text{O}$  are sediments, and rocks weathered or altered by surface waters at low temperatures. Clearly such protoliths have increasingly been involved in genesis of younger magmas on Earth.

The variability of  $^{18}\text{O}$  in terrestrial magmas should not be seen on planets lacking a liquid water hydrosphere or processes of magmatic recycling of surface rocks.

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**Figure 1.** Compilation of  $^{18}\text{O}(\text{Zrc})$  vs. age for zircons from over 1100 rocks with published age. Oxygen isotope ratios were analyzed by laser fluorination at the University of Wisconsin (most samples) or in situ by ion microprobe at the University of Edinburgh (Jack Hills zircons). Samples range in age from 4400 to 0.2 Ma and come from many terranes on seven continents. A remarkable uniformity is seen in the Archean, values cluster near the mantle ( $^{18}\text{O}(\text{Zc}) = 5.3 \pm 0.3\text{‰}$ ) with some values as high as 7.5 due to recycling of supracrustal material. High  $^{18}\text{O}$ , above 8‰ becomes common after 1.5 Ga, reflecting recycling of high  $^{18}\text{O}$  sediment and maturation of the crust. (Valley, Lackey, Basei, Bindeman, Clechenko, Ferreira, King, Peck, Sial, Sinha, and Spicuzza, unpd)



**THE OXYGEN ISOTOPE COMPOSITION OF THE MOON: IMPLICATIONS FOR PLANET FORMATION.** U. Wiechert<sup>1</sup>, <sup>1</sup>Institute for Isotope Geology and Mineral Resources, ETH-Zentrum NO, 8092 Zürich, Switzerland. E-mail address: [wiechert@erdw.ethz.ch](mailto:wiechert@erdw.ethz.ch)

**Introduction:** The Moon is widely considered to have formed during a collision between the proto-Earth and a Mars-sized planet (named Theia). Assuming this model to be correct the Moon was formed from materials from the proto-Earth, Theia and any additional material added later. Oxygen isotope variations in differentiated planetary bodies like the Earth, Mars or the HED parent body are largely mass-dependent, i.e. the data define a characteristic line with a slope of  $\sim 0.52$  in a graph of  $^{17}\text{O}$  vs.  $^{18}\text{O}$ . In general, different parent bodies define distinct parallel trends reflecting different bulk compositions for the parent bodies. The differences are usually expressed as  $^{17}\text{O}$ , which is the deviation from the mass-dependent fractionation trend defined by terrestrial samples in per mil  $^{17}\text{O}$ . The first oxygen isotope data for lunar samples published by Clayton and Mayeda [1] fell along a linear array overlapping with the terrestrial samples. However, these early oxygen isotope data for the Moon have a large range of  $\sim 0.3\%$  which may reflect some isotopic heterogeneity of the Moon. Therefore, lunar samples have been re-investigated with a high precision  $\text{CO}_2$  laser fluorination method [2].

**Results:** With this method the oxygen isotopic composition of 31 lunar samples averaged  $^{17}\text{O}=0 \pm 0.005\%$  (3 sigma standard error of the mean). Even at this very high precision no resolvable difference between the Earth and Moon is detectable despite the fact that oxygen isotopes are very heterogeneous in the solar system. The simplest explanation for an identical oxygen isotope composition would be that the proportions of material from the impactor and the proto-Earth were identical in the Earth and Moon. Most giant impact simulations indicate that the majority of the material that formed the Moon originated from Theia rather than the proto-Earth. Given that the most of the Earth was already built by the time of the Giant Impact the proportions cannot be the same. The only explanation that is consistent with Giant Impact simulations is that Theia and the proto-Earth had identical or very similar oxygen isotope compositions.

**Discussion:** If Theia and the Earth formed from raw materials that were identical in oxygen isotopes, why then are they so different in terms of their chemical composition? For example the Moon and Earth have very different depletion in volatiles and the lunar mantle has a high FeO content. Some of this could result from the giant impact or differentiation of the

proto-Earth, Theia, the Moon, or the present Earth. Comparing the Moon with other planetary bodies such as Mars or the HED parent body indicates that the Fe content of the lunar mantle is "normal" and the Fe content of the terrestrial mantle is unusually low. Therefore, the difference might be completely related to more protracted and extensive terrestrial core formation, but this is far from settled.

Another striking difference between the Earth and Moon is the strong depletion of the Moon in volatile elements compared with the Earth. Potassium isotopes have been used to argue that the depletion of alkalis and other volatiles in the inner solar system must have occurred during the condensation of precursor dust from a hot stage of the solar nebula [3]. This seems to favor an origin of Theia from material with a higher degree of depletion in volatiles. However, recently it has been argued that the Moon lost volatiles during its accretion [4]. The latter is supported by the timing of the moderate volatile element loss for the Moon  $>10$  Myrs after cooling of the solar nebula [5]. This is inconsistent with models that assume a very early volatile loss. In fact, it supports the view that moderately volatile elements have been lost during accretion. Therefore, the oxygen isotope composition of the Moon provide evidence that objects as different as the Moon and Earth have been made out of an identical mix of material. The mechanism of volatile element loss without corresponding mass-dependent fractionation is the subject of ongoing research.

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# OXYGEN ISOTOPE COMPOSITION OF EUCRITES AND IMPLICATIONS FOR THE FORMATION OF CRUST ON THE HED PARENT BODY. U. Wiechert<sup>1</sup>, A. N. Halliday<sup>1</sup>, H. Palme<sup>2</sup> and D. Rumble<sup>3</sup>,

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**Introduction:** Oxygen isotopes are a powerful tool for assessing the provenance of early solar system material [1]. This approach can be used to assess the number of parent bodies of differentiated silicate meteorites, or achondrites. The largest group among these meteorites are howardites, eucrites and diogenites, often referred to as HED meteorites. To evaluate whether all HEDs formed on a single or several parent bodies we have determined precise abundances of <sup>16</sup>O, <sup>17</sup>O and <sup>18</sup>O for 34 HED meteorites using a CO<sub>2</sub> laser fluorination technique. This also allows us to evaluate whether eucrites formed by melting poorly mixed primitive material [2] or a homogeneous reservoir such as might be produced in a magma ocean [3].

**Results:** The <sup>17</sup>O' values of 6 howardites, 24 eucrites, and 4 diogenites range from -0.245 to -0.057‰. HEDs, excluding Ibitira, fall along a mass-dependent fractionation line that lies at -0.219 ± 0.002‰ (2 standard error mean) relative to the terrestrial fractionation line (TFL) whereas Ibitira falls 0.064‰ below the terrestrial fractionation line. Also individual analyses of Caldera, Pasamonte, and ALHA78132 are different, with 95% confidence, from the HED average.

**Discussion:** The oxygen isotope data provide evidence that most meteorites are derived from a common, well-mixed pool. The eucrites (without Ibitira, Pasamonte, Caldera, and ALHA78132) and diogenites average <sup>17</sup>O' = -0.219 ± 0.004‰ and <sup>17</sup>O' = -0.224 ± 0.006‰ (2 mean error) respectively and are indistinguishable from each other. Therefore, there is no evidence that eucrites and diogenites are from systematically distinct parent bodies or reservoirs. However, whether this "oxygen pool" that is sampled by most of the HED meteorites is representative of an entire parent body is now unclear because there are resolvable differences for the basaltic eucrites Ibitira, Pasamonte, ALHA78132, and Caldera. If one considers the <sup>17</sup>O to be a parent body "fingerprint" [1] these meteorites could come from an asteroid that is distinct from the main group parent body. One would then expect differences in chemical compositions and these should be largest between the most distinct eucrite, Ibitira, and the main group eucrites, but this is not observed.

A second possibility is that the HED parent body is heterogeneous in oxygen isotopes. In this case oxygen

isotopes allow us to draw some conclusions on the petrogenesis of eucrites.

Stolper [2] presented a model for eucrite petrogenesis in which basaltic eucrites represent primary partial melts of an undifferentiated parent body. In this model the parent body underwent minimal heating and only localized melting occurred. If the HED parent body was never homogenized completely then some primary oxygen isotope heterogeneity should be found among eucrites, which is inconsistent with the oxygen isotopes for most eucrites presented in this study. Others have proposed that the HED mantle underwent a global magma ocean stage [3]. Such a magma ocean would help explain why extremely early basaltic eucrites are derived from a parent body that appears to have been completely homogeneous in terms of oxygen isotopes within a few million years of the start of the solar system. However, such a model is in conflict with the oxygen isotope composition of Ibitira, Caldera, Pasamonte, and ALHA78132.

Gosh and McSween [5] suggested a model for the evolution of Vesta which assumes partial melting of the silicate mantle and low temperatures for near-surface layers. The thickness of an outer unaltered layer decreases with increasing degree of melting and, for 25% melting, the outer 10 km of the asteroid never reached melting temperatures. Such outer layers could have retained some isotopic heterogeneity. In contrast to the global magma ocean scenario [3] this model predicts mixing and perfect homogenisation of the interior but also allows for some oxygen isotope heterogeneity in an outer layer of the HED parent body. In this model crust formed by extrusion of basaltic melts at the surface. Therefore, it also explains why no anorthositic crust has been found on Vesta, which may be a much better model for the formation of early crust on Earth than the Moon.

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# THE ROLE OF WATER IN DETERMINING THE OXYGEN ISOTOPIC COMPOSITION OF PLANETS.

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**Introduction:** It is becoming increasingly likely that reactions between water and rock (and rock melts) were the primary by which planetesimals, and eventually terrestrial planets, obtained their oxygen isotopic signatures. Two processes were responsible. One is photochemistry in the early solar nebula [1, 2]. The other is reactions between liquid water ice melt and rocks within protoasteroid environments [3, 4].

**Photochemistry:** Self shielding of CO to produce oxygen depleted in <sup>16</sup>O [5] is sure to have occurred at some level in the diffuse regions of the early solar nebula. Calculations show that attenuation of a stellar flux of UV photons illuminating the disk surface is small enough that many Earth masses of oxygen with large depletions in <sup>16</sup>O relative to the starting materials would have been produced above and below the mid-plane of the early solar nebula over time scales > 10<sup>3</sup> yrs. The most likely sink for the <sup>17</sup>O and <sup>18</sup>O-rich oxygen liberated by photolysis of CO (Q\*) would have been adsorption onto solid dust grains followed by surface reactions to produce water. Settling of these dust grains and radial transport toward the accreting star brings this source of <sup>16</sup>O-depleted oxygen into the nascent inner solar system where it can react with gases, minerals, and liquids that form planet precursors.

Many observations are consistent with photodissociation of CO in the diffuse regions of the solar nebula as an explanation for the slope-1 line in oxygen isotope  $\delta$ - $\delta$  space. It accounts for the fact that H<sub>2</sub>O was almost certainly depleted in <sup>16</sup>O (enriched in H<sub>2</sub>Q\*) relative to silicates and other metal oxides in the solar system. Reactions between H<sub>2</sub>Q\* and CO in the inner solar nebula (at higher T) would not affect the slope-1 relationship in three isotope space because the mass-dependent fractionation between H<sub>2</sub>O and CO is small at all relevant temperatures. Production in the outer solar nebula also provides a natural explanation for the correlation between <sup>16</sup>O and refractory nature of solids.

**Asteroid hydrology:** Much of the <sup>16</sup>O-poor oxygen isotopic signal incurred by photochemistry may have been imparted to protoplanetary material in the inner solar system by melt-vapor exchange. Later, this same <sup>16</sup>O-poor water condensed with rock materials to form planetesimals. Upon internal heating, the <sup>16</sup>O-poor water must have melted. There is abundant evi-

dence that liquid and/or vaporous water was present within the parent bodies of primitive chondrite meteorites. There is also evidence that water would have flowed through the bodies [3, 6]. Analysis of the consequences of water-rock reactions during flow shows that  $\Delta^{17}\text{O}$  of the <sup>16</sup>O-poor water would have been reduced during incipient alteration. In regions of large time-integrated fluxes the  $\Delta^{17}\text{O}$  of the rock would begin to rise. These expectations are born out by the carbonaceous chondrite oxygen isotope data.

**Conclusions:** The oxygen isotopic composition of solar system bodies records of a long history of reactions between protoplanetary material and water that was <sup>16</sup>O-poor relative to the bulk of solar system material. This history began photochemistry prior to the formation of rocky bodies and continued through the geological evolution of planetesimals.

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